Incorporating Product Design into the Development of New Refrigerants

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Abstract

This study proposes the use of product design in the development of new refrigerants. Product design involves the use of consumer preference functions as described by Bagajewicz (2007). Consumer preference functions relate the satisfaction of consumers to different refrigerants based on their properties. The properties examined in this study were toxicity, flammability, explosion potential, global warming potential, ozone depletion potential and efficiency.

The method used to solve for new refrigerants was achieved using an iterative method based on group contribution theory. A detailed discussion of group contribution theory and the possible refrigerants generated is presented. The refrigerants were then ranked based on their efficiency estimated as $\Delta H_{ve}/C_p$, as presented by Sahinidis (2003). After completion of this, the new refrigerants were ranked using consumer preferences. The ranking system was drastically altered by the use of consumer preference functions. This is indicative of advantages to using a different object function when ranking possible refrigerants.

Another estimation performed in this study was the market potential. The target market was the automotive market because it offers high volumes of sales. The market potential was estimated to be 14.2 thousand metric tons of refrigerant need per year. This indicates that an alternative refrigerant will have the potential to generate high profits as the industry standard R-134a is phased out.

Introduction

The phase-out of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) has instigated a search for new refrigerant molecules that have similar characteristics to the CFCs and HCFCs, but are not damaging to the environment. A stable, non-toxic, nonflammable, highly efficient refrigerant with no potential to contribute to global warming and ozone depletion would be ideal.

Perfluorocarbons (compounds consisting of solely carbon and fluorine) offered a possible alternative because fluorine is not thought to contribute to depletion of the ozone, but even these compounds are seen as doomed by the technical community (Calm 1998). This study focuses on comparing refrigerant alternatives with the incorporation of product design. Product design offers a method for selecting refrigerants based not only on physical properties, but the preferences of consumers.

1 Background

More than 2000 years ago the Romans and Greeks sent expeditions to the mountains in the winter to collect snow, which was then stored for use as a food preservative (Winnick 1997). Hundreds of years ago, ice was made in the dry regions of Egypt and India by allowing air to evaporate to the open night sky (Winnick 1997). Now, refrigerators, air conditioned cars, offices and homes, cold-brewed beer, refrigerated transport, temperature-controlled medical environments, and even computer chip cooling are made possible by specially designed fluids operating in mechanical refrigeration cycles.

The first mechanically produced cooling system was developed in England in 1834 (Winnick 1997). The process later became known as vapor compression. Basically, a refrigerator or air conditioner is nothing more than a heat pump whose job is to remove heat from a low temperature source and reject heat to a higher temper sink (Winnick 1997). Figure 1 shows the basic vapor compression refrigeration cycle.

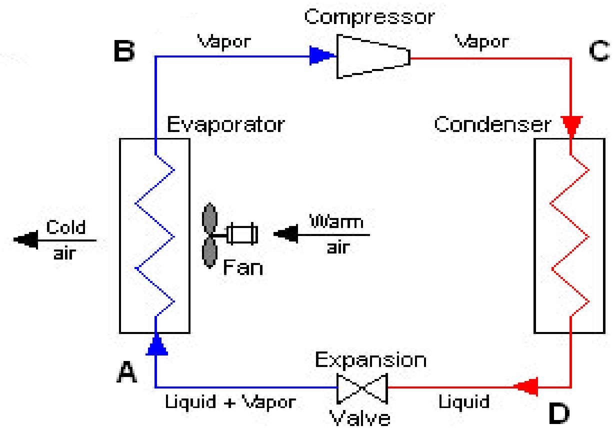

Figure 1[1] – Basic Vapor Compression Refrigeration Cycle

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[1] *Vapor-Compression Refrigeration*. Answers.com. 4/27/2007 <http://www.answers.com/topic/vapor-compression-refrigeration>.

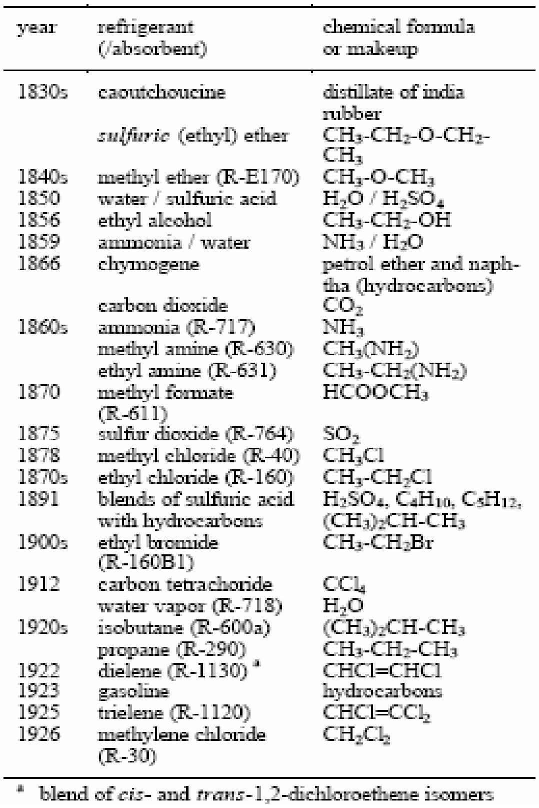
In this process, cooling is achieved through the Joule-Thompson expansion of a fluid through an expansion valve. In figure 1, the refrigerant leaves the expansion valve as a saturated vapor-liquid mix (A). The refrigerant then enters the evaporator, which converts the saturated mix to a saturated vapor (B). The refrigerant is then compressed and leaves the compressor as a superheated vapor (C). Then a condenser converts the superheated vapor into a saturated liquid (D). The saturated liquid then flows through the expansion valve and the cycle repeats.

The process shown in Figure 1 was the model used to evaluate the refrigerants in this report because it is employed in common appliances and air-conditioning units. Sections 1.1 through 1.4 discuss the types of fluids that have been used as refrigerants.

1.1 First Generation: 1830-1926

The first refrigerants were introduced in 1830s with the invention of the vapor compression cycle. The chosen refrigerants were based on availability. These refrigerants were often highly toxic, flammable and some were even highly reactive (Calm 1998). Some of these early refrigerants survived, but most are no longer used. Ammonia is an example of a first generation refrigerant that survived. Although ammonia is toxic, it remains the preferred refrigerant in some industrial operations (Calm 1998). Table 1 lists these early refrigerants and the time of their introduction.

Table 1[2]: Refrigerants 1830 - 1926



year	refrigerant (/absorbent)	chemical formula or makeup
1830s	caoutchoucine	distillate of india rubber
	sulfuric (ethyl) ether	CH_3-CH_2-O-CH_2-CH_3
1840s	methyl ether (R-E170)	CH_3-O-CH_3
1850	water / sulfuric acid	H_2O / H_2SO_4
1856	ethyl alcohol	CH_3-CH_2-OH
1859	ammonia / water	NH_3 / H_2O
1866	chymogene	petrol ether and naphtha (hydrocarbons)
	carbon dioxide	CO_2
1860s	ammonia (R-717)	NH_3
	methyl amine (R-630)	$CH_3(NH_2)$
	ethyl amine (R-631)	CH_3-$CH_2(NH_2)$
1870	methyl formate (R-611)	$HCOOCH_3$
1875	sulfur dioxide (R-764)	SO_2
1878	methyl chloride (R-40)	CH_3Cl
1870s	ethyl chloride (R-160)	CH_3-CH_2Cl
1891	blends of sulfuric acid with hydrocarbons	H_2SO_4, C_4H_{10}, C_5H_{12}, $(CH_3)_2CH$-CH_3
1900s	ethyl bromide (R-160B1)	CH_3-CH_2Br
1912	carbon tetrachoride	CCl_4
	water vapor (R-718)	H_2O
1920s	isobutane (R-600a)	$(CH_3)_2CH$-CH_3
	propane (R-290)	CH_3-CH_2-CH_3
1922	dielene (R-1130) [a]	CHCl=CHCl
1923	gasoline	hydrocarbons
1925	trielene (R-1120)	$CHCl$=CCl_2
1926	methylene chloride (R-30)	CH_2Cl_2

[a] blend of *cis*- and *trans*-1,2-dichloroethene isomers

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[2] Calm, James M. and David A. Didion. "Trade-Offs in Refrigerant Selections: Past, Present and Future." *Int. J. Refrig., 21, 308 (1998).*

1.2 Second Generation: 1930-1990

The second generation refrigerants focused on reducing toxicity and flammability. In the 1920’s, General Motors Corporation hired Thomas Midgley to find a refrigerant with a low toxicity, low flammability, good stability, and an atmospheric boiling point between –40 and 32℉ (Lawrence 2003). It took him and his associates three days. They synthesized all 15 combinations of one carbon with various combinations of chlorine, fluorine, and hydrogen. They finally chose dichlorodifluoromethane (Freon) as having the most desirable characteristics, thus introducing the first chlorofluorocarbons (Lawrence 2003). One of the most famous displays of its non-toxic properties occurred when Thomas Midgely filled his lungs with Freon and blew out a candle (Lawrence 2003).

While synthesizing Freon, Midgley and his colleagues made three interesting observations. First, flammability decreases from left to right for the eight elements shown in figure 2. Second, toxicity generally decreases from the heavy elements at the bottom to the lighter elements at the top. Lastly, every known refrigerant at the time was made from combinations of the elements shown in figure 2 (Calm 1998).

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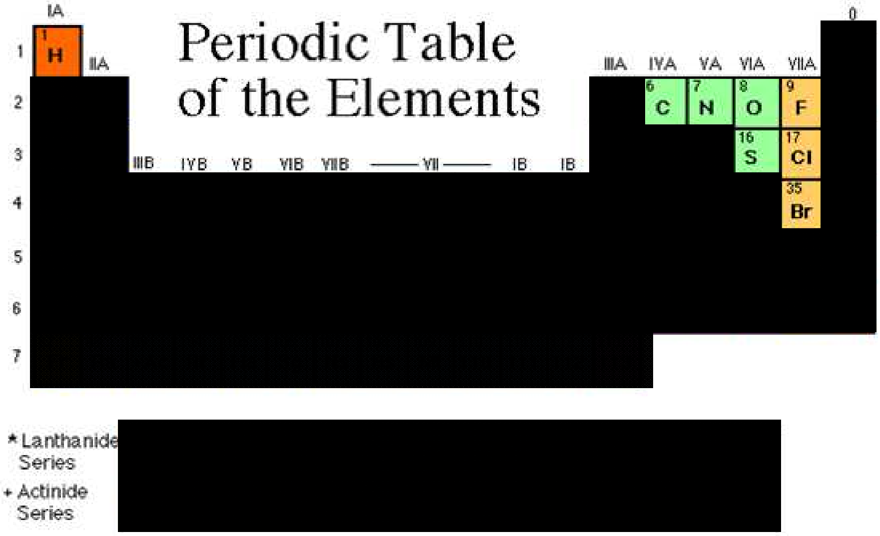

Figure 2 – Periodic Table with Midgley's Highlighted Elements

1.3 Third Generation: 1990-2010

The third generation refrigerants focused on protecting the ozone. The chlorofluorocarbons (CFC’s) were found to be a catalyst in the decomposition of ozone (O_3). Ozone is naturally and constantly formed and decomposed in the atmosphere because of high energy UV light. When exposed to UV light, the CFC’s decompose leaving a radical chlorine atom which readily reacts with ozone. Researches found that replacing one of the chlorine atoms, in a CFC, with a hydrogen atom makes a much more stable refrigerant in the stratospheric ozone layer (Lawrence 2003). This discovery led to the introduction of hydrochlorofluorocarbons (HCFCs). They have about 90% less ozone depleting potential (Lawrence 2003). HCFCs are now used as a replacement to CFC’s, but they still contribute to ozone depletion and are therefore scheduled for phase-out.

1.4 Fourth Generation: 2010-

A fourth generation refrigerant would ideally be efficient, nonflammable and non toxic with good stability, no global warming potential (GWP) and no ozone depletion potential (ODP). But the outlook for discovery or synthesis of these ideal refrigerants is extremely unlikely. Therefore, trade-offs among desired objectives are necessary to achieve balanced solutions (Calm 1998). Interestingly, many first generation refrigerants are being examined as possible fourth generation refrigerants (Calm 2007). Figure 3 shows a diagram displaying the progression of refrigerants throughout time.

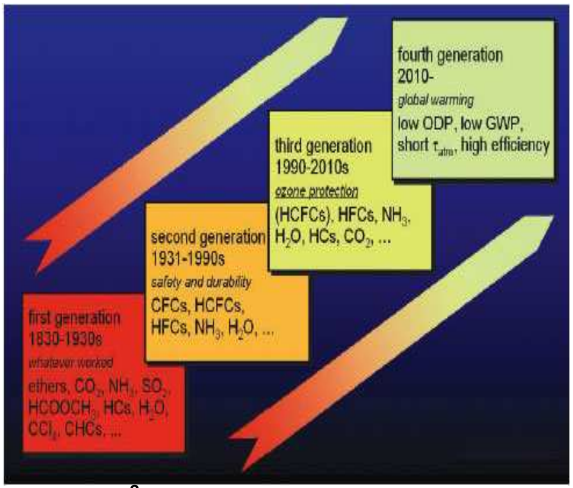

Figure 3[3] – Refrigerant Fluid Progression

1.5 Refrigerant Phase-out Schedule

1.5.1 The Montreal Protocol

Following the discovery of the Antarctic ozone hole in late 1985, governments recognized the need for stronger measures to reduce the production and consumption of a number of CFCs (UNEP 2004). The Montreal Protocol on Substances that Deplete the Ozone Layer was adopted on 16 September 1987 at the Headquarters of the International Civil Aviation Organization in Montreal (UNEP 2004). The Protocol came into force on January 1st, 1989, when it was ratified by 29 countries and the EEC. Since then several other countries have ratified it (UNEP 2004).

The Montreal Protocol established requirements that began the worldwide phase-out of CFCs. In 1992, this protocol was amended to include HCFCs in the phase-out schedule. The phase-out schedule for HCFCs begins in 2003 and continues until 2030. Table 2 displays the HCFC phase-out schedule (EPA 2007).

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[3] Calm, James M. and Glenn C. Hourahan. *Refrigerant Data Update*. January 2007. Heating/Piping/Air Conditioning Engineering. Feb. 7, 2007 <http://www.hpac.com/Issue/Article/44475/Refrigerant Data Update>.

Table 2[4]: Phase-out Schedule for HCFCs

Year	Production Reductions (%)
2003	The amount of all HCFCs that can be produced nationwide must be reduced by 35.0%
2010	The amount of all HCFCs that can be produced nationwide must be reduced by 65.0%
2015	The amount of all HCFCs that can be produced nationwide must be reduced by 90.0%
2020	The amount of all HCFCs that can be produced nationwide must be reduced by 99.5%
2030	No HCFCs can be produced

1.5.2 The Kyoto Protocol

In 1992 the United Nations Framework Convention on Climate Change (UNFCCC) met in Rio de Janeiro at the Earth Summit to discuss the potential of human contributions to global climate change though CO_2 and other greenhouse gas emissions, which include methane, $NO_{X,}$ nitrous oxide, CFCs and HFCFs .Initially, a voluntary goal was established to reduce greenhouse gas emissions below 1990 levels (PEW 1998).

Later, the participating countries recognized that stronger action was needed and established the Kyoto Protocol. The Kyoto protocol aims to reduce greenhouse gas emissions to 5.2% below 1990 levels by 2012. Over 100 countries have ratified this treaty, but the U.S. still has not ratified the agreement. Many U.S. cities and some states have ratified the treaty, but the United States, as a whole, has neglected to ratify the treaty. Owing to the current debate on global warming and the increases in state and city participation, it is assumed that the US will eventually ratify the Kyoto Treaty (PEW 1998).

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[4] *What you Should Know about Refrigerants when Purchasing or Repairing a Residential A/C System or Heat Pump*. Jan. 29, 2007. Environmental Protection Agency. Jan. 29th, 2007 <http://www.epa.gov/ozone/title6/phaseout/22phaseout.html>.

2 The Use of Consumer Preference Functions in Refrigerant Design

In this study, the design of new refrigerants was incorporated with consumer preferences functions. The purpose of using consumer preference functions was to calculate the demand for a new product when it is in competition with an existing product. Once the demand has been predicted, the profitability of producing a new product can be determined. This assessment is necessary because producing the best product may not be profitable as suggested by Bagajewicz (2007). The following equation, derived from microeconomics, was used to calculate the demand for new refrigerants. In this equation, the variable β is the only variable developed from consumer preference functions.

Equation 1 – Demand for a New Product

$$\phi(d_1) = p_1 d_1 - \left(\frac{\alpha}{\beta}\right)^{\rho} p_2 \left[\frac{Y - p_1 d_1}{p_2}\right]^{1-\rho} d_1^{\rho} = 0$$

Where: d_1 is the demand for the new product
p_1 is the price for the new product
p_2 is the price for the existing product
Y is the market potential
ρ is a constant that was set to a value of 0.76
α is the consumer awareness of the new product as a function of time
β is the parameter used to relate respective consumer preferences

2.1 Consumer Preference Functions

Consumer preference functions are used to predict consumer reactions to different design properties. In this case, consumer preference functions were used to predict consumer reactions to refrigerant properties. The properties for examination were flammability, toxicity, explosion potential, efficiency, global warming potential, and ozone depletion potential.

The development of consumer preferences can be conducted in two ways. The first, and least accurate, involves estimation. An engineer or economist can conduct market research and estimate the reactions that consumers will have to the properties of interest. The second way involves an in-depth survey that polls consumers about the properties of interest. This method is far more accurate because consumers actually participate in the process.

In this study, the consumer preferences had to be estimated because the resources for an in-depth survey were not available (although it was not employed, a survey was prepared and is attached in the appendix). This is an unfortunate drawback, but it does not nullify the validity of the consumer preference functions that were developed. They offer insight into designing refrigerants using consumer preferences.

2.1.1 Development of β using Consumer Preference Functions

In equation 1, the variable of greatest interest to engineers is β because it can be manipulated by varying different design parameters (Bagajewicz 2007). The goal is to design products that minimize β. The following equation shows how β was developed.

Equation 2 – Respective Consumer Preferences

$$\beta = \frac{H_2}{H_1}$$

In the preceding equation, H_2 is the consumer preference function of the existing product and H_1 is the consumer preference of the new product. The following equation shows how H_2 and H_1 were developed.

Equation 3 – Consumer Preference Function

$$H_i = \sum \omega_i y_i$$

Where: ω_i is the weight of the refrigerant property
y_i is the property score of each refrigerant property

The most important variable in the preceding equation is the property score, y_i, because it changes for alternative refrigerants; whereas ω_i remains constant. The desired outcome is that a minimum value for β can be achieved by investigating multiple refrigerants. This is based on the assumption that many of the refrigerants examined will have different property scores; thus changing the value of β.

Property scores are developed using a two step process. First, a refrigerant property is related to options that a non scientific participant can understand. This is important because the participants of the surveys must be able to identify with refrigerant properties. Participants are asked to list, on a percentage basis, how satisfied they are with each of the options given for a refrigerant property. Figure 4 depicts the expected satisfaction curve for the provided efficiency options. In figure 4, a property score of one indicates that the consumer is 100% satisfied and a property score of zero indicates that the consumer is 0% satisfied.

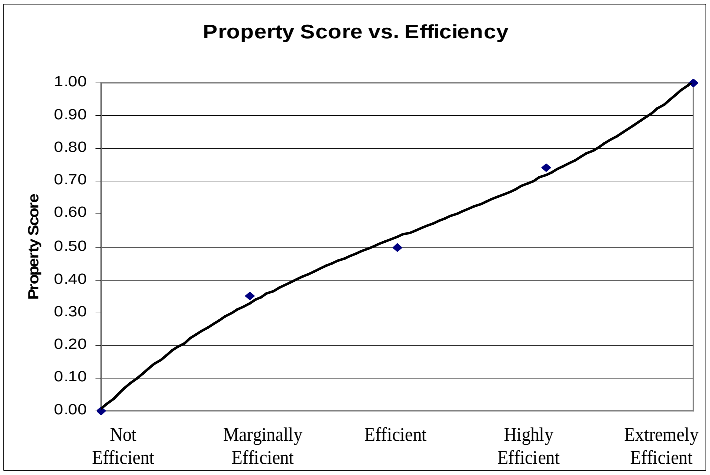


Figure 4 – Satisfaction vs. Efficiency

After generating the satisfaction curve from consumer preferences, the x-axis is changed so that it can be used in the design process. Figure 5 displays the evolution of the satisfaction curve in figure 4 into a relationship between consumer satisfaction and a measurable design variable. Figures 6-15 were developed using the same methods described for figures 4 and 5.

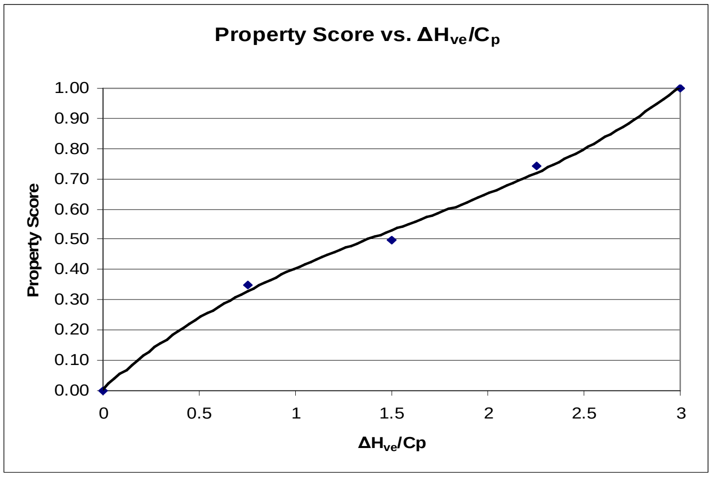


Figure 5 – Property Score vs. $\Delta H_{ve}/C_p$

Figures 6 & 7 display how this was performed for flammability.

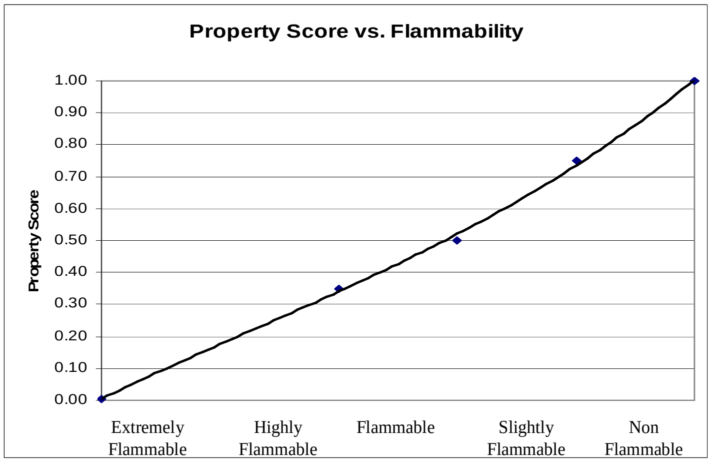


Figure 6 – Satisfaction vs. Flammability

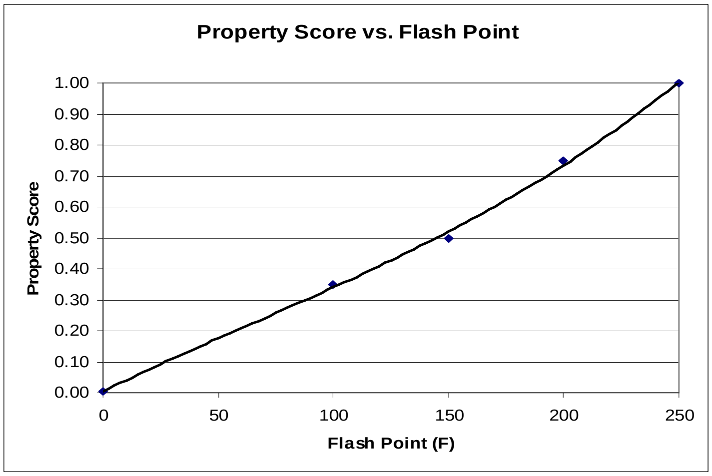


Figure 7 – Property Score vs. Flash Point

Figures 8 & 9 display how this was performed for toxicity.

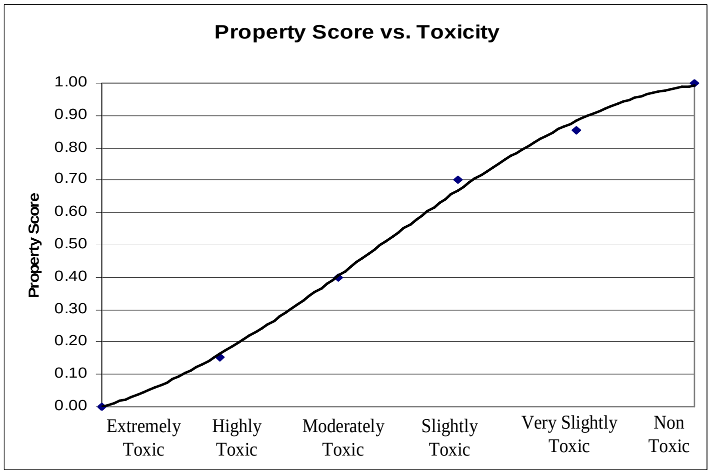


Figure 8 – Satisfaction vs. Toxicity

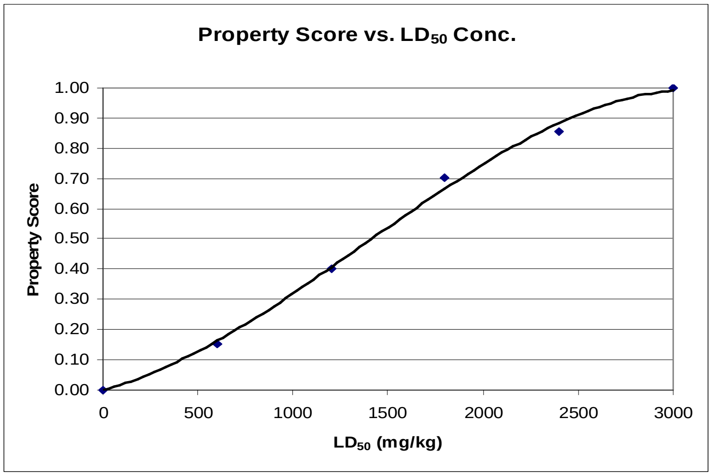


Figure 9 – Property Score vs. LD_{50} Conc.

Figures 10 & 11 demonstrate how this was performed for explosion potential.

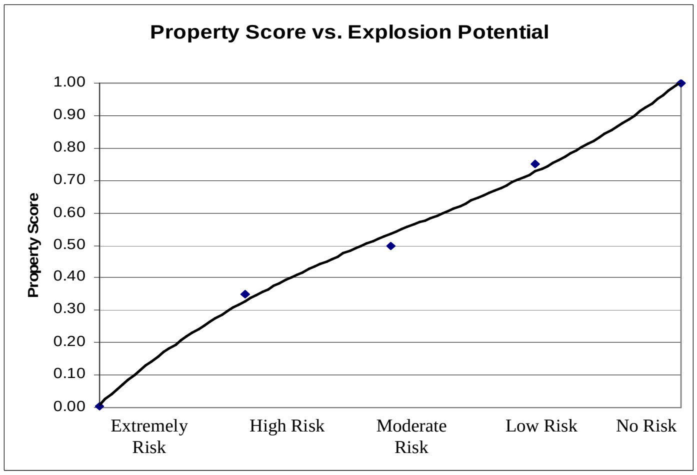


Figure 10 – Satisfaction vs. Explosion Potential

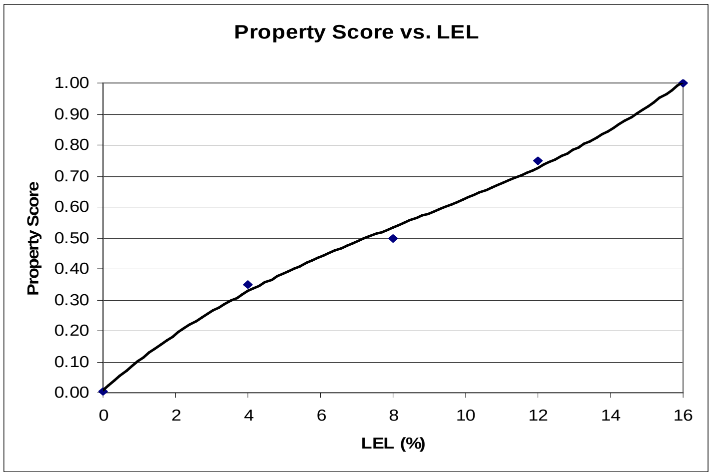


Figure 11 – Property Score vs. Lower Explosion Limit

Figures 12 & 13 display how this was performed for global warming potential.

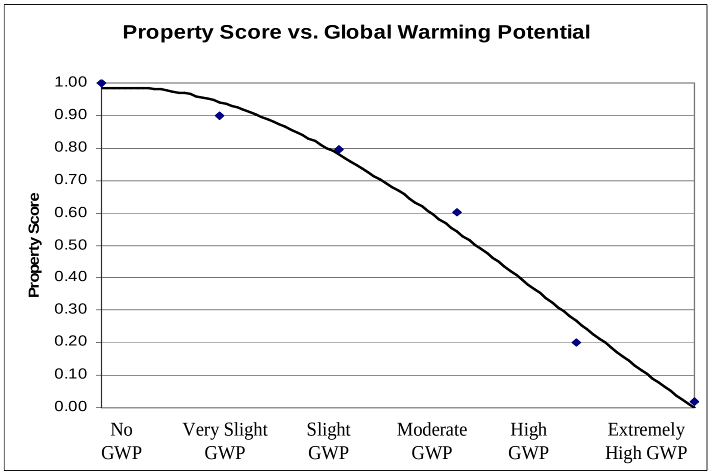


Figure 12 – Satisfaction vs. Global Warming Potential

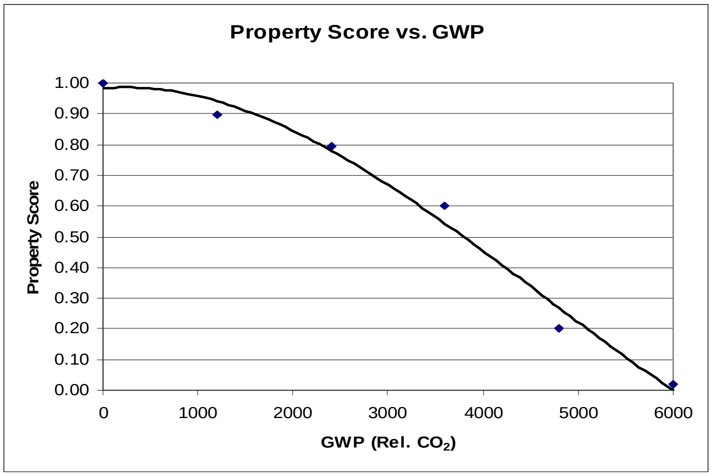


Figure 13 – Property Score vs. GWP relative to CO_2

Figures 14 &15 display how this was performed for the ozone depletion potential.

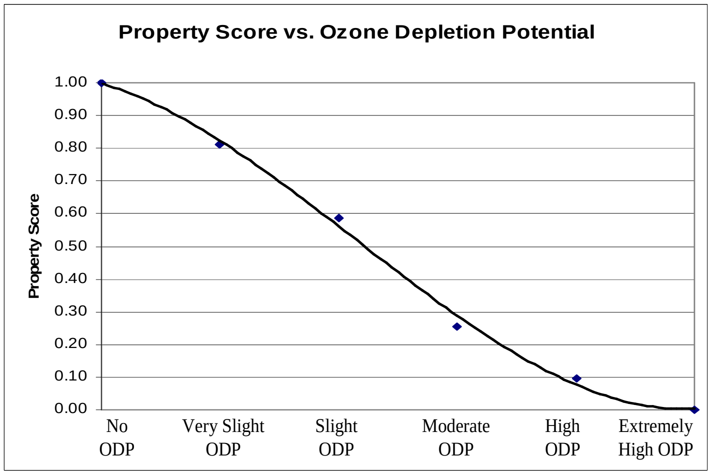


Figure 14 – Satisfaction vs. Ozone Depletion Potential

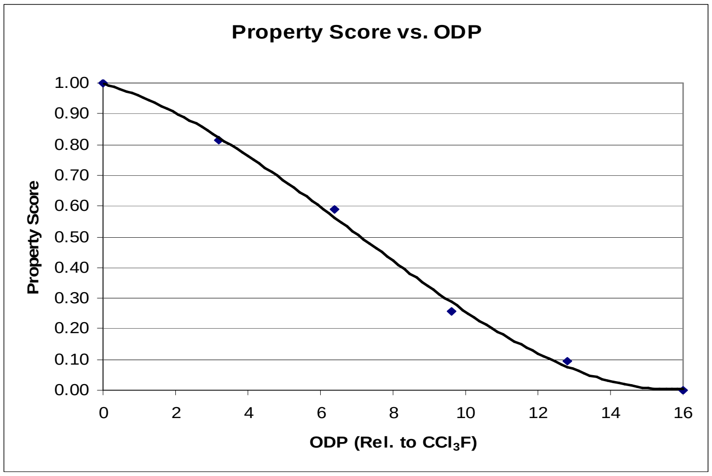


Figure 15 – Property Score vs. ODP relative to CCl_3F (R-11)

After relating the y_i to a measurable design variable, it is necessary to develop the respective weights (ω_i) of each refrigerant property. To do this, participants in the previously mentioned survey would be asked to rank refrigerant properties based on importance. A rank of 10 would mean that the refrigerant property is extremely important to the consumer and a rank of 1 would infer that the refrigerant property is unimportant. The rankings would then be normalized and used for the respective weights of each property. It is important to note that the respective weights must sum to 1. Figure 16 displays the expected weights for each refrigerant property.

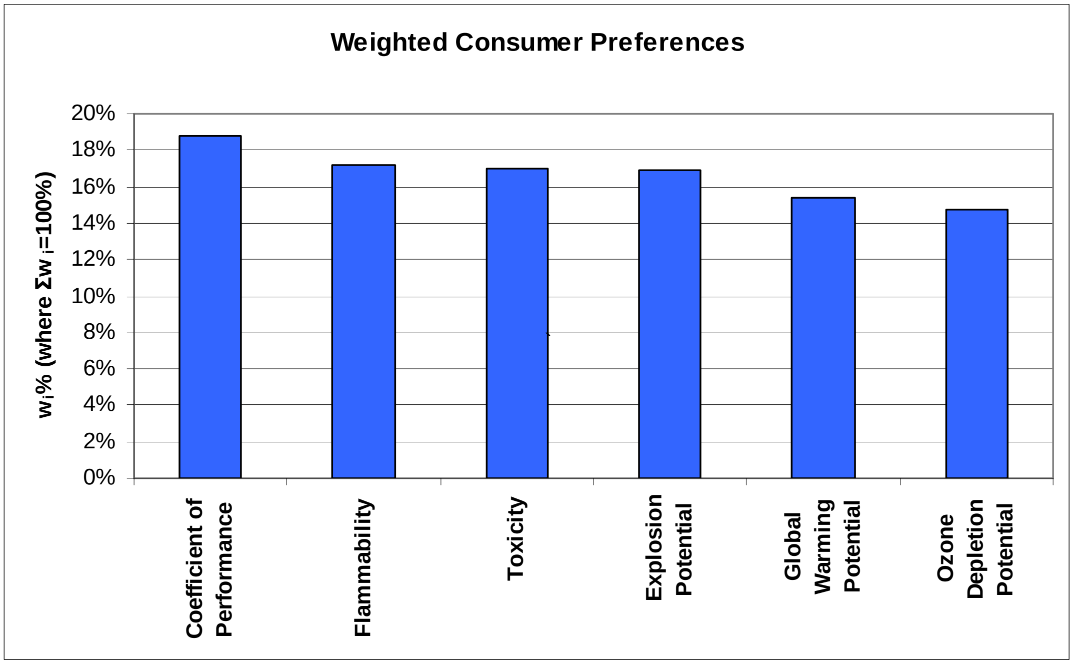


Figure 16 – Respective Weights of Refrigerant Properties

2.2 Developing α

α is the consumer awareness of the new refrigerant as a function of time. Initially, the consumer will be completely unaware of the new refrigerant. This is assumed to be when production of the new refrigerant begins. As time progress, consumers will gradually become aware of the new refrigerant. Figure 18 displays how the value of α varies with time.

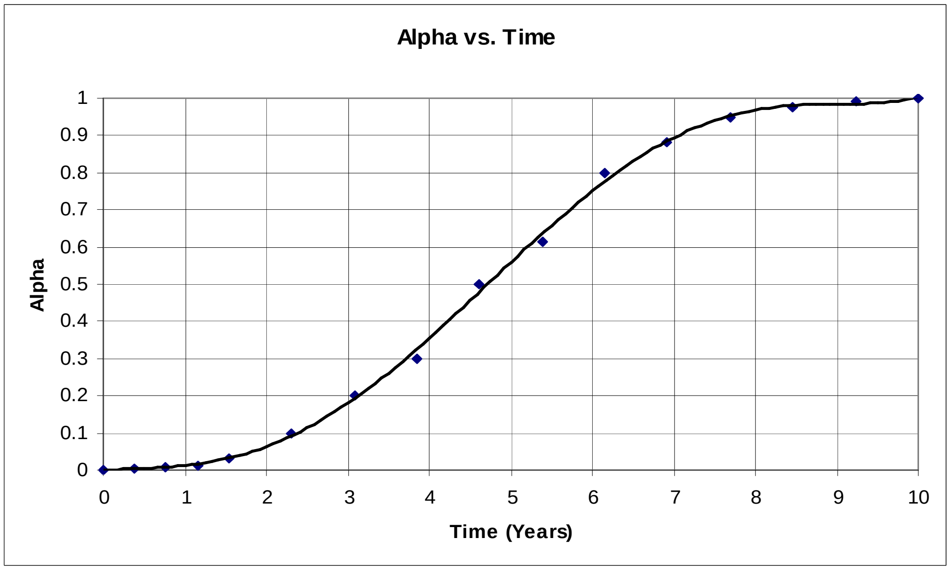


Figure 17 – Alpha vs. Time (yrs)

In Figure 19, the pink (top) line represents how the value of α can be increased by increased advertising. By increasing the consumer awareness of the new refrigerant, the demand at earlier production years will be higher. This will affect initial sales more dramatically than sales during later years. When calculating demand, it was assumed that no advertising would be utilized.

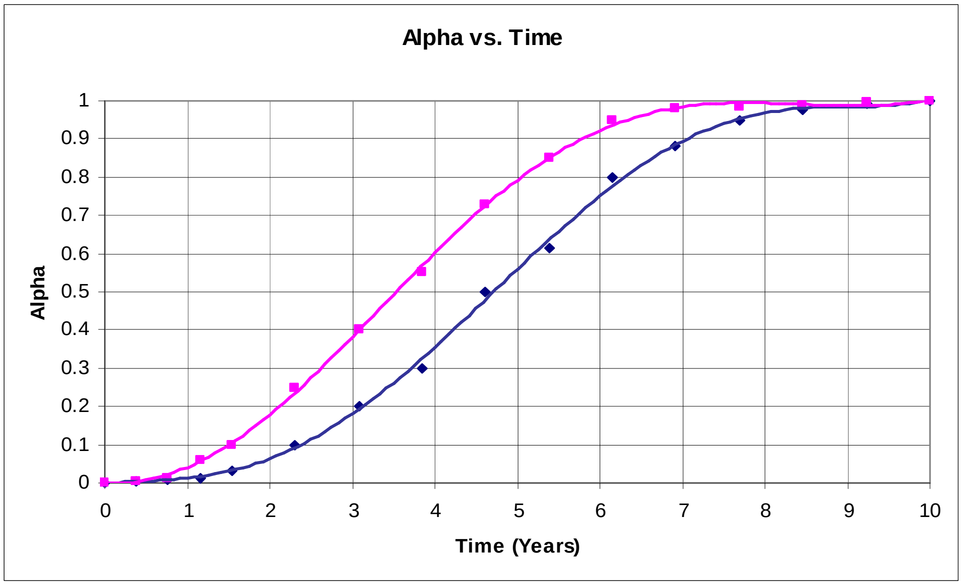


Figure 18 – Effect of advertising on the value of α

2.3 Estimating the Market Potential (Y)

Before the market potential can be estimated, a target market must be defined. The following sections provide information on two markets of interest.

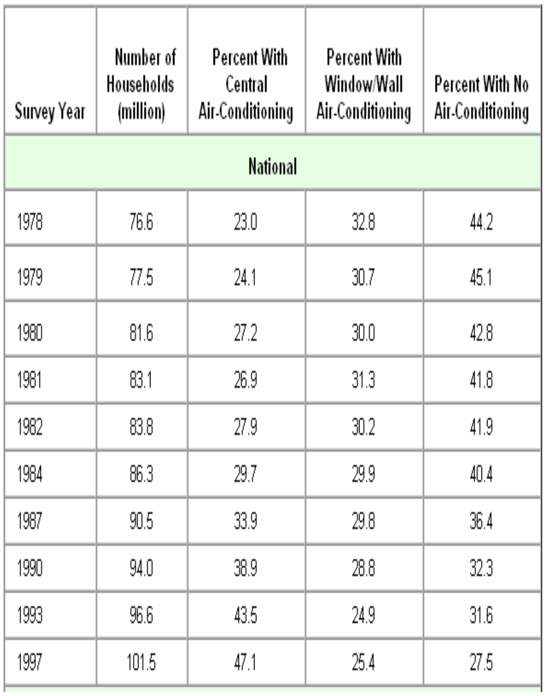
2.3.1 Refrigerant Markets

The air-conditioning and refrigeration industry is in the midst of an unprecedented transition, catalyzed by environmental concerns with the impacts of refrigerant emissions (Calm 1998). Coupling the phase-out schedules with increasing environmental concerns offers an excellent market to exploit. As older, undesirable refrigerants leave the market, more desirable, environmentally friendly refrigerants will gain more of the market share. This drives the design and development of new refrigerants. In this study, the two markets examined for the release of a new refrigerant were the residential air-conditioning market and the automotive air-conditioning market. The following sections provide more details on each respective market.

2.3.1.1 Residential Air Conditioning

In 1997, forty-seven percent of the households in the US had Central Air Conditioning (DOE 2000). Table 3 displays the number of households in United States and the percentages of these households that have air-conditioning. Based on the trend in Table 3, it can be assumed that the number of household with air conditioning is likely to increase.

Table 3[5]: Households with air conditioning



Survey Year	Number of Households (million)	Percent With Central Air-Conditioning	Percent With Window/Wall Air-Conditioning	Percent With No Air-Conditioning
National				
1978	76.6	23.0	32.8	44.2
1979	77.5	24.1	30.7	45.1
1980	81.6	27.2	30.0	42.8
1981	83.1	26.9	31.3	41.8
1982	83.8	27.9	30.2	41.9
1984	86.3	29.7	29.9	40.4
1987	90.5	33.9	29.8	36.4
1990	94.0	38.9	28.8	32.3
1993	96.6	43.5	24.9	31.6
1997	101.5	47.1	25.4	27.5

Table 3 provides information regarding the number of units in circulation, but it does not provide information concerning the volume of units sold per year. Figure 4 displays the volume of air conditioners sold in the US from 1999 to 2004. The volume of air conditioners is estimated to reach 10.7 million units by 2008 (Snapshot Int. 2004). This demonstrates that the residential market has the potential for a high volume of refrigerant sales.

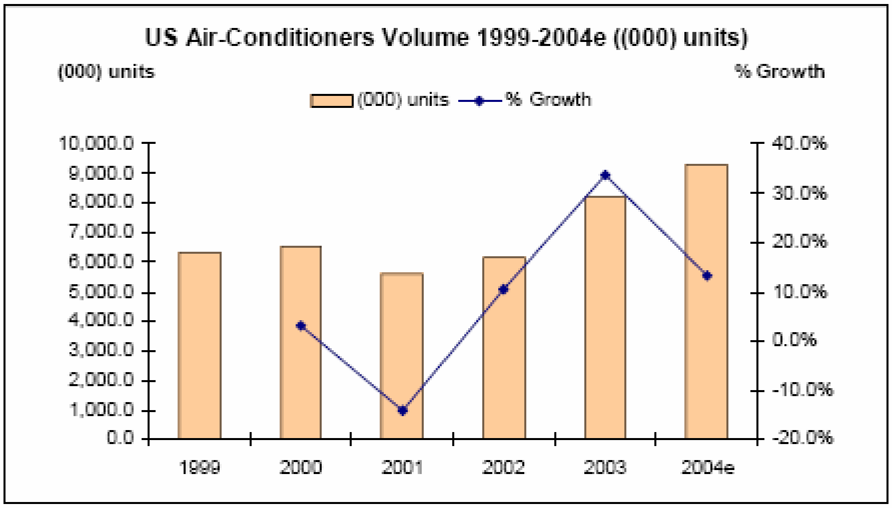


Figure 19[6] – Air Conditioning Units Sold Per Year

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[5] Trends in Residential Air-Conditioning Usage from 1978 to 1997. July 24, 2000. US Department of Energy. Feb 11th, 2007 <http://www.eia.doe.gov/emeu/consumptionbriefs/recs/actrends/recs_ac_trends.html>.

2.3.1.2 Automotive Air Conditioning

The residential market is large, but the automotive market is larger. In the United States, automotive sales totaled nearly 17 million vehicles in 2005. As well as targeting the US, the worldwide market for automotive air conditioning could be exploited. Figure 4 depicts the automotive sales for several industrialized countries in 2005.

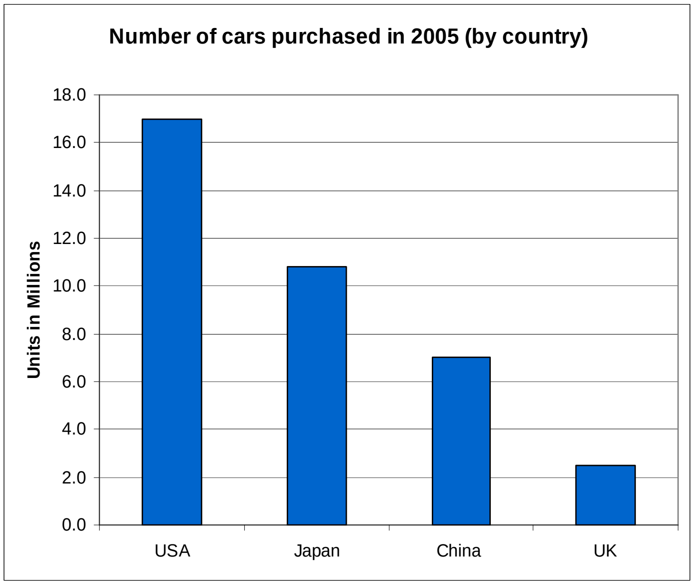

Figure 20 – Cars sold by country

In this study, the automotive industry was targeted for a replacement refrigerant. This decision was based on the higher volume of automotive sales per year. As such, the theoretical refrigerants will be compared to the industry standard HCFC-134a (UNFCCC 2007). HCFC is also known as R-134a or 1,1,1,2-tetrafluoroethane.

2.3.2 Estimating the Market Potential (Y) for the Automotive Market

In 2000, 17.394 million new cars were sold in the United States (Taylor 2006). If it assumed that all of these automobiles have refrigeration systems and these refrigeration systems all require approximately 24oz. to operate, then approximately 14.2 thousand metric tons of R-134a would have been used in automobile refrigeration systems in the year 2000. This number can then be compared with data obtained from the United Nations Framework Convention on Climate Change (UNFCCC 2007).

The UNFCCC provides information pertaining to yearly refrigerant production rates and the amount of refrigerant released into the atmosphere. The UNFCCC only includes information from participating countries. These countries are Australia, Columbia, the European Union and its member states, Japan, Switzerland and the United States. Table 4 illustrates the data provided by the UNFCCC, but it is important

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[6] Air Conditioners 2004. July 2004. Snapshot International. Feb. 11th, 2007 <http://dx.doi.org/10.1337/us080034>.

to note that this includes the production of R-134a for uses in the production of polystyrene. R-134a may be used in other applications, but these were not listed.

Table 4: Annual R-134a production and atmospheric release

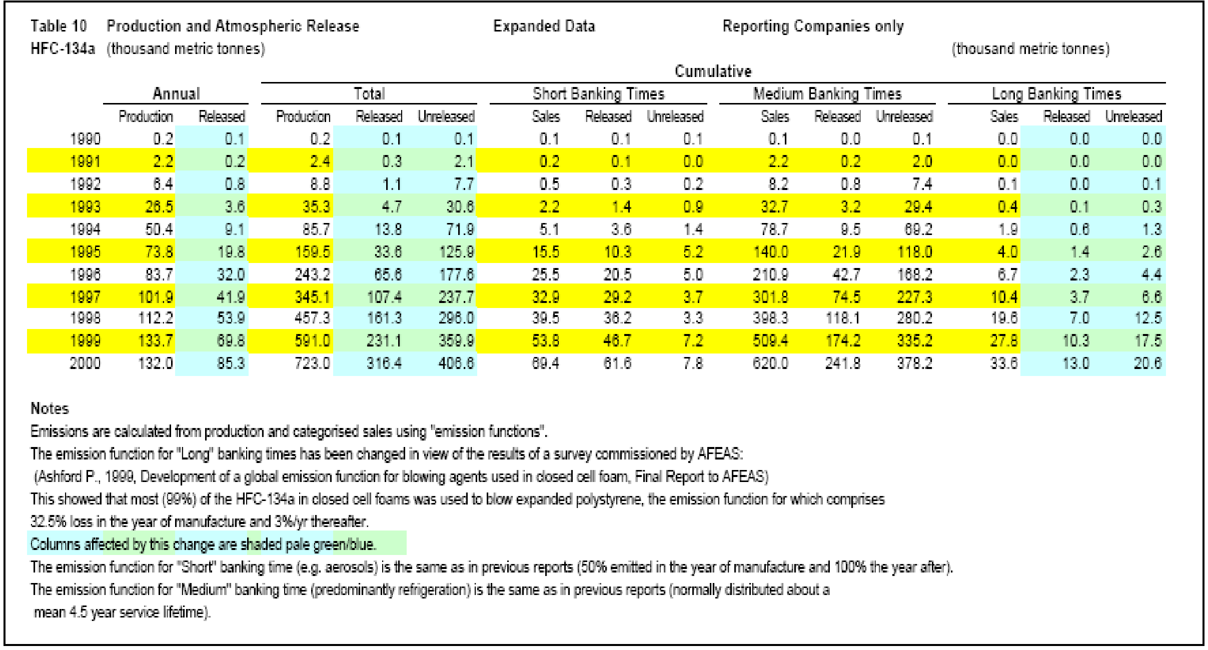

Table 10 Production and Atmospheric Release Expanded Data Reporting Companies only

HFC-134a (thousand metric tonnes) (thousand metric tonnes)

	Annual		Total			Cumulative Short Banking Times			Cumulative Medium Banking Times			Cumulative Long Banking Times		
	Production	Released	Production	Released	Unreleased	Sales	Released	Unreleased	Sales	Released	Unreleased	Sales	Released	Unreleased
1990	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.0	0.0
1991	2.2	0.2	2.4	0.3	2.1	0.2	0.1	0.0	2.2	0.2	2.0	0.0	0.0	0.0
1992	6.4	0.8	8.8	1.1	7.7	0.5	0.3	0.2	8.2	0.8	7.4	0.1	0.0	0.1
1993	26.5	3.6	35.3	4.7	30.6	2.2	1.4	0.9	32.7	3.2	29.4	0.4	0.1	0.3
1994	50.4	9.1	85.7	13.8	71.9	5.1	3.6	1.4	78.7	9.5	69.2	1.9	0.6	1.3
1995	73.8	19.8	159.5	33.6	125.9	15.5	10.3	5.2	140.0	21.9	118.0	4.0	1.4	2.6
1996	83.7	32.0	243.2	65.6	177.6	25.5	20.5	5.0	210.9	42.7	168.2	6.7	2.3	4.4
1997	101.9	41.9	345.1	107.4	237.7	32.9	29.2	3.7	301.8	74.5	227.3	10.4	3.7	6.6
1998	112.2	53.9	457.3	161.3	296.0	39.5	36.2	3.3	398.3	118.1	280.2	19.6	7.0	12.5
1999	133.7	69.8	591.0	231.1	359.9	53.8	46.7	7.2	509.4	174.2	335.2	27.8	10.3	17.5
2000	132.0	85.3	723.0	316.4	406.6	69.4	61.6	7.8	620.0	241.8	378.2	33.6	13.0	20.6

Notes

Emissions are calculated from production and categorised sales using "emission functions".

The emission function for "Long" banking times has been changed in view of the results of a survey commissioned by AFEAS:

(Ashford P., 1999, Development of a global emission function for blowing agents used in closed cell foam, Final Report to AFEAS)

This showed that most (99%) of the HFC-134a in closed cell foams was used to blow expanded polystyrene, the emission function for which comprises 32.5% loss in the year of manufacture and 3%/yr thereafter.

Columns affected by this change are shaded pale green/blue.

The emission function for "Short" banking time (e.g. aerosols) is the same as in previous reports (50% emitted in the year of manufacture and 100% the year after).

The emission function for "Medium" banking time (predominantly refrigeration) is the same as in previous reports (normally distributed about a mean 4.5 year service lifetime).

When the US automotive needs are compared to the worldwide production, it is determined that the US automotive need accounts for approximately 10% of the provided value. This value seems reasonable and was therefore used to calculate the market potential.

One additional assumption must be made before the market potential can be explicitly stated. The final assumption made was that the automotive market potential will remain constant at 14.2 thousand metric tons per year. This assumption is justified because automotive sales remained essentially constant from 1999-2005 (Taylor 2006). For this reason, the market potential for R-134a is assumed to be 14.2 thousand metric tons per year.

2.4 Competitor Product Price (p_2)

The product price of R-134a (p_2) was estimated at 10.00 \$/kg. This value was obtained from Lenz Sales & Distributing, Inc (Lenz 2006). The distribution size used for pricing information was the 12oz. canister.

3 Design of New Refrigerants Based on Consumer Preference Functions and the Chosen Market

There are two methods that could have been employed in the search for new refrigerants. The first method would involve compiling lists of known molecules that have properties suited for refrigeration processes. The possible refrigerants would then be compared using properties such as boiling point, coefficient of performance, toxicity, GWP, ODP, and flammability. The refrigerant with the most desirable characteristics would then be selected as the best available alternative and production could commence after laboratory testing. The drawback to this method is that new or unknown molecules would not be included in the list for comparison.

To account for this, group contribution theory coupled with computer modeling was used to generate a list of all potential refrigerant molecules. These molecules were then compared in two different ways. They were first compared using an object function developed by Sahinidis (2003). Then, they were compared using respective consumer preferences described in equation 2.

3.1 Group Contribution Theory

For the estimation of physical and thermodynamic properties of pure compounds, group contribution methods are the most widely used. In these methods, the property of a compound is estimated as a summation of the contributions of simple first-order groups which can occur in the molecular structure. They provide the important advantage of quick estimates without requiring substantial computational resources (Constantinou 1994). In this study, the same physical and thermodynamic relations were as in Joback and Reid (1987).

Group contribution theory was developed by observation of existing molecules as a way to predict the basic characteristics of any molecule. Observation divides the existing molecules into groups called functional groups. Statistical averages are then recorded in tables to be used as references. The statistical data of each functional group can then be used to estimate the characteristics of a molecule formed from the functional groups.

3.1.1 Functional Groups used in this study

Table 5 displays the functional groups that were used in this study. In the following table, a dash (-) represents and single bond. The equal sign (=) denotes a double bond, (R) represents a ring bonding site, and (>) represents two single bonds. These functional groups were selected because they were all common in existing refrigerants.

Table 5: Functional Groups Examined in this Study

Acyclic Groups	Cyclic Groups	Halogen Groups	Oxygen Groups	Nitrogen Groups	Sulfur Groups
-CH3	**R-CH2-R**	**-F**	**-OH**	**-NH2**	**-SH**
-CH2-	**2R>CH-R**	**-Cl**	**-O-**	**>NH**	**-S-**
>CH-	**2R>C<2R**	**-Br**	**R-O-R**	**2R>NH**	**R-S-R**
>C<	**R=CH-R**	**-I**	**>CO**	**>N-**	
=CH2	**R=C<2R**		**2R>CO**	**R=N-**	
=CH-			**-CHO**	**-CN**	
=C<			**-COOH**	**-NO2**	
=C=			**-COO-**		
			=O		

3.2 Computer Modeling Using the Selected Functional Groups

Initially, a user interface for mathematical optimization was employed to find the optimum solution for a specified objective function. The advantages of this method are as follows: the model calculates only options that lead to a more likely solution and solutions are found in a relatively short period of time. However, the model requires a good initial guess and a database of chemicals and properties. The database necessary for accurate evaluation of the objective function could not be sufficiently automated in the user interface.

Because of this drawback, a different approach was utilized. This approach used an iterative method. The iterative method produced a list of all the possible refrigerant molecules. The possible refrigerants were developed from differing combinations of the functional groups listed in table 5. The advantage of this method is that every possible solution is found and then these solutions can then be compared in multiple ways.

A spreadsheet, which incorporated the iterative module, searched every possible combination within the constraints.

3.3 Predicting Physical Properties of Theoretical Refrigerants

The iterative model employed provided a list of theoretical refrigerants, but properties of these refrigerants were needed to develop a ranking system. To do this, physical properties of the molecules were needed. The following equations, presented by Joback (1987) were used to calculate the physical properties of the generated theoretical refrigerants.

Equation 4 – Boiling Temperature

$$T_b = 198.21 + \sum_{i=1}^{N} n_i * T_{bi}$$

Where: n_i = Number of Functional Groups present
T_b= Boiling temperature
T_{bi}= Contribution of group i to boiling temperature

Equation 5 – Critical Temperature

$$T_c = \frac{T_b}{(0.584 + 0.965 * \sum_{i=1}^{N} n_i * T_{ci} - \left(\sum_{i=1}^{N} n_i * T_{ci} \right)^2}$$

Where: T_c= Critical temperature
T_{ci}= Contribution of group i to critical temperature

Equation 6 – Critical Pressure

$$P_c = \frac{1}{\left(0.113 + 0.0032 * \sum_{i=1}^{N} n_i * a_i - \sum_{i=1}^{N} n_i * P_{ci} \right)^2}$$

Where: a_i=number of atoms in group i
P_{ci}= contribution of group i to critical pressure

Equation 7 – Ideal Gas Heat Capacity at Average Temperature

$$C_{p0a} = \sum_{i=1}^{N} n_i * C_{p0ai} - 37.93 + \left(\sum_{i=1}^{N} n_i * C_{p0bi} - 0.21 \right) * T_{avg}$$
$$+ \left(\sum_{i=1}^{N} n_i * C_{p0ci} - 3.91 * 10^{-4} \right) * T_{avg}^2$$
$$+ \left(\sum_{i=1}^{N} n_i * C_{p0di} - 2.06 * 10^{-7} \right) * T_{avg}^3$$

Where: T_{avg}= average temperature (user defined)
C_{p0ai}=*a* contribution to heat capacity
C_{p0bi}=*b* contribution to heat capacity
C_{p0ci}=*c* contribution to heat capacity
C_{p0di}=*d* contribution to heat capacity at average temperature

Equation 8 – Reduced Boiling Temperature

$$T_{br} = \frac{T_b}{T_c}$$

Equation 9 – Reduced Average Temperature

$$T_{avgr} = \frac{T_{ave}}{T_c}$$

Equation 10 – Reduced Condensing Temperature

$$T_{cndr} = \frac{T_{cnd}}{T_c}$$

Where: T_{cnd} = Condensing temperature in the refrigerant cycle

Equation 11 – Reduced Evaporating Temperature

$$T_{evpr} = \frac{T_{evp}}{T_c}$$

Where: T_{evp} = Evaporating temperature in the refrigerant cycle

Equation 12 – Accentric Factor (ω)

$$\alpha = -5.97214 - \ln\left(\frac{P_c}{1.013}\right) + \frac{6.09648}{T_{br}} + 1.28862 * \ln(T_{br}) - 0.169347 * T_{br}^6$$

$$\beta = 15.2518 - \frac{15.6875}{T_{br}} - 13.4721 * \ln(T_{br}) + 0.43577 * T_{br}^6$$

$$\omega = \frac{\alpha}{\beta}$$

Equation 13 – Liquid Heat Capacity

$$C_{pla} = \frac{1}{4.1868} * \left\{ C_{p0a} + 8.314* \left[1.45 + \frac{0.45}{1-T_{avgr}} + 0.25*\omega* \left(17.11 + 25.2* \frac{\left(1-T_{avgr}\right)^{1/3}}{T_{avgr}} + \frac{1.742}{\left(1-T_{avgr}\right)} \right) \right] \right\}$$

Equation 14 – Enthalpy of Vaporization at Boiling Temperature

$$\Delta H_{vb} = 1.093 * R * T_c * T_{br} * \left(\frac{\ln\left(P_c\right) - 1.013}{0.930 - T_{br}} \right)$$

The Riedel method (Poling 2001) was used to estimate the enthalpy of vaporization at boiling temperature because the method used by Joback (1987) yielded poor results. This method was advantageous because it is a function of Tc, Tb, and Pc and these values are easily calculated using equations 4-6.

Equation 15 – Reduced Vapor Pressure at Condensing Temperature P_{VPCR}

$$h = \frac{T_{br} * \ln\left(P_c / 1.013\right)}{1 - T_{br}}$$

$$G = 0.4835 + 0.4605 * h$$

$$k = \frac{h/G - \left(1 + T_{br}\right)}{\left(3 + T_{br}\right)\left(1 - T_{br}\right)^2}$$

$$Ln(P_{PVCR}) = \frac{-G}{T_{cndr}} \left[1 - T_{cndr}^2 + k(3 + T_{cndr})(1 - T_{cndr})^3 \right]$$

Equation 16 – Reduced Vapor Pressure at Evaporating Temperature

$$Ln(P_{PVER}) = \frac{-G}{T_{evpr}} \left[1 - T_{evpr}^2 + k(3 + T_{evpr})(1 - T_{evpr})^3 \right]$$

Equation 17 – Vapor Pressure at Condensing Temperature

$$P_{vpc} = P_{vpcr} P_c$$

Equation 18 – Vapor Pressure at Evaporating Temperature

$$P_{vpe} = P_{vper} P_c$$

3.3.1 Structural Constraints

Structural constraints were incorporated into the iterative module to ensure that the combinations of functional groups formed feasible or realistic molecules. The six structural constraints employed are as follows:

1. There must be an even number of functional groups with an odd number of bonding sites, (i.e. 1 or 3 bonding sites.)
2. Functional groups must be able to be connected to form one molecule.
3. Because two bonding sites are needed to make one bond, the total number of bonding sites should be even.
4. The number of functional groups of each bond type should be even.
5. When the set of functional groups contain two or more bond types, a transitional group must exist. The transitional group is one that contains at least two different bonding site types (i.e. =CH- contains both a single and a double bonding site.)
6. Every branch should have an edge or end cap. The end cap is a functional group with only one bonding site; it essentially closes the molecule.

3.3.2 Physical Constraints

Physical constraints based on the molecular size and vapor pressure limitations. The use of functional requires that at least two groups are combined to make one molecule. Additionally, observations of our results showed that no molecules that met the thermodynamic constraints exceeded ten functional groups.

To prevent a leak into the compressor system, the minimum vapor pressure at evaporation is set to 1 bar. The vapor pressure of a potential refrigerant should also fall within the mechanical limitations of the vapor compressor. The maximum vapor pressure at condensation is set to 10 bar.

3.4 Limitations of Group Contribution Theory

Group contribution theory is helpful when predicting physical properties, but it has its drawbacks. One of these drawbacks is that it does not accurately predict physical properties for some molecules. To illustrate this, the estimated values for the boiling temperature, critical temperature and critical pressure were compared to actual values listed for molecules. This has only been performed for molecules with literature values, but it is apparent that group contribution fails drastically for some molecules. Table 6 depicts the error associated with the properties examined.

Table 6: Error Using Group Contribution Theory

	T_b	T_c	P_c
Maximum Error	47%	32%	36%
Minimum Error	0.4%	1.1%	0.5%
Average Error	16%	14%	12%

3.5 Selected Objective Function for Refrigerant Ranking

The objective function chosen for ranking the refrigerant molecules is shown in the following equation.

Equation 19 – Objective Function Selected for Ranking Refrigerants

$$Obj = \frac{\Delta H_{ve}}{C_{pla}}$$

This objective function was proposed by Sahinidis (2003). The theory behind this objective function is that a fluid with a large heat of vaporization has the ability to remove a larger amount of heat from the surrounding environment (i.e. to cool more air per unit mass) and the smaller liquid heat capacity reduces the amount of refrigerant vapor generated in the expansion valve (Sahinidis 2003). Theoretically, this objective function predicts the efficiency of the refrigerant, but this theory could not be tested.

Table 7 displays the top 20 theoretical refrigerants. Many of these compounds already exist, but several are unknown compounds.

Table 7: Ranked Refrigerants using the Objective Function Proposed by Sahinidis (2003)

Ranking	Molecule	$\Delta H_{ve}/C_p$
1	CH_2=CH-Cl	2.12
2	CH_2=CH-F	1.73
3	CH2=CFCl	1.72
4	CH_3 -CH=CH_2	1.60
5	CH_2=C=CH-F	1.51
6	CH_2=CH-O-F	1.46
7	Cl_2	1.38
8	CH_2=CF_2	1.37
9	F-Br	1.35
10	CH_2=CCH_3F	1.34
11	CH_2=CH-CH_2-F	1.31
12	CH_2=C=CF_2	1.28
13	CH_2=C=C=C=O	1.25
14	FSH	1.24
15	CH2=C(-F)-O-F	1.24
16	FNH_2	1.24
17	cyc(CH=CH-CH2)	1.24
18	cyc(CH=CH-O)	1.23
19	O=CH-Br	1.17
20	CH2=CH-C(=O)-F	1.16
R-134a	R134a	0.56

Table 8 displays how the ranking system changes when the consumer preference functions described in section 2.1.1. The property scores used to calculate the consumer preference functions in table 8 were developed from data available in literature sources.

Table 8: The Effect β has on the Ranking System

Chemical Formula	$H = \Sigma x_i y_{ij}$	$\beta = H_2/H_1$	Ranking using $\Delta H_{ve}/C_p$
CH2=CH-F	0.61	1.39	2
CH3 -CH=CH2	0.61	1.39	4
CH2=CF2	0.51	1.68	8
CH2=CH-Cl	0.50	1.69	1
CH2=CFCl	0.49	1.75	3
CH2=C=CH-F	0.40	2.13	5
CH2=CH-O-F	0.40	2.14	6
CH2=CH-C(=O)-F	0.40	2.14	20
Cl2	0.40	2.15	7
F-Br	0.39	2.17	9
CH2=CCH3F	0.39	2.17	10
CH2=CH-CH2-F	0.39	2.18	11
CH2=C=CF2	0.39	2.18	12
CH2=C=C=C=O	0.39	2.19	13
FSH	0.39	2.19	14
CH2=C(-F)-O-F	0.39	2.19	15
FNH2	0.39	2.19	16
cyc(CH=CH-CH2)	0.39	2.19	17
cyc(CH=CH-O)	0.39	2.20	18
O=CH-Br	0.38	2.22	19
R134a	$H_2 = 0.85$	-	-

3.5.1 Correlation with Molecular Weight

One observation produced from this study was the correlation between the objective function and the molecular weight. It was assumed that lighter molecules generally make better refrigerant and figure 7 affirms this assumption. Therefore, future efforts should be concentrated in research molecules with lower molecular weights rather than heavier molecules.

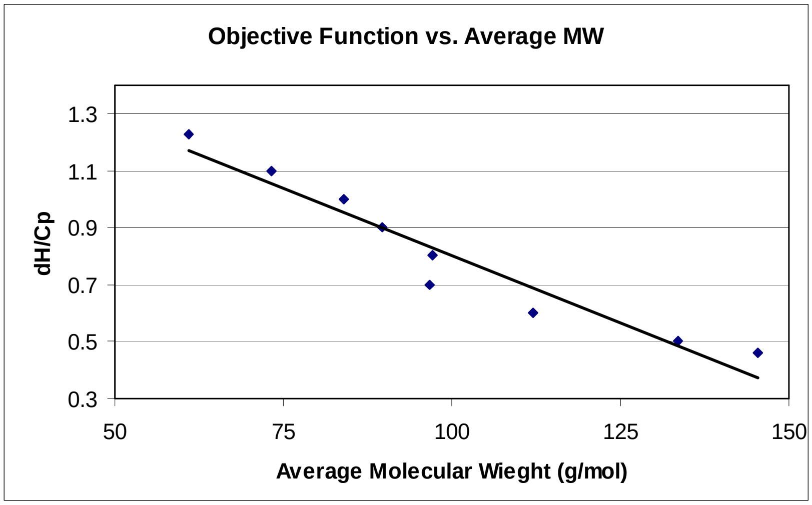

Figure 21 – $\Delta H/C_p$ vs. molecular weight

4 Conclusions

The incorporation of consumer preference functions into the design of new refrigerants was the objective in this study. The advantage of using consumer preference functions, instead of efficiency, to rank lists of possible refrigerants has been effectively demonstrated. Tables 7 and 8 show how drastically the ranking system changed when consumer preference functions were used.

The objective of the study was a success, but it is important to consider one of the limitations in the widely accepted design procedure used for development of new refrigerants.

Group contribution theory, the most common method used to predict pure component physical data, is not a good way to predict properties for a wide range of molecules. It predicts data well for some molecules, but drastically fails for other molecules. This is a severe design limitation because it excludes some of the possible molecules from examination. To account for this, it is recommended that a different method of calculating these physical properties be developed.

5 Recommendations

Recommendations for the improvement of this study are as follows:

1.) Develop correlations to relate data obtained from models to consumer preference functions. Relationships could be developed to relate properties that can be found from the empirical data to those exclusive to an individual molecule.
2.) Link spreadsheets to databases to quickly search through molecules. Not all properties can be examined from a molecule’s empirical formula or structure. Many databases, in periodicals, for potential refrigerant molecules are available for possible refrigerants. These databases could eliminate error caused by property estimation.
3.) A large scale survey needs to be performed. A large scale random survey is needed to find actual consumer preferences to refrigerant properties.

4.) More structural constraints need to be developed. Some molecular structures pass the filters in the iterative method, but do not exist in reality.
5.) Considering refrigerant blends would create many more options for refrigerant solutions.
6.) Lastly, a study needs to be performed in the laboratory. The laboratory setting offers the benefit of being able to measure data for synthesized refrigerants. In this way, more accurate correlations for group contributions or efficiency could be developed.

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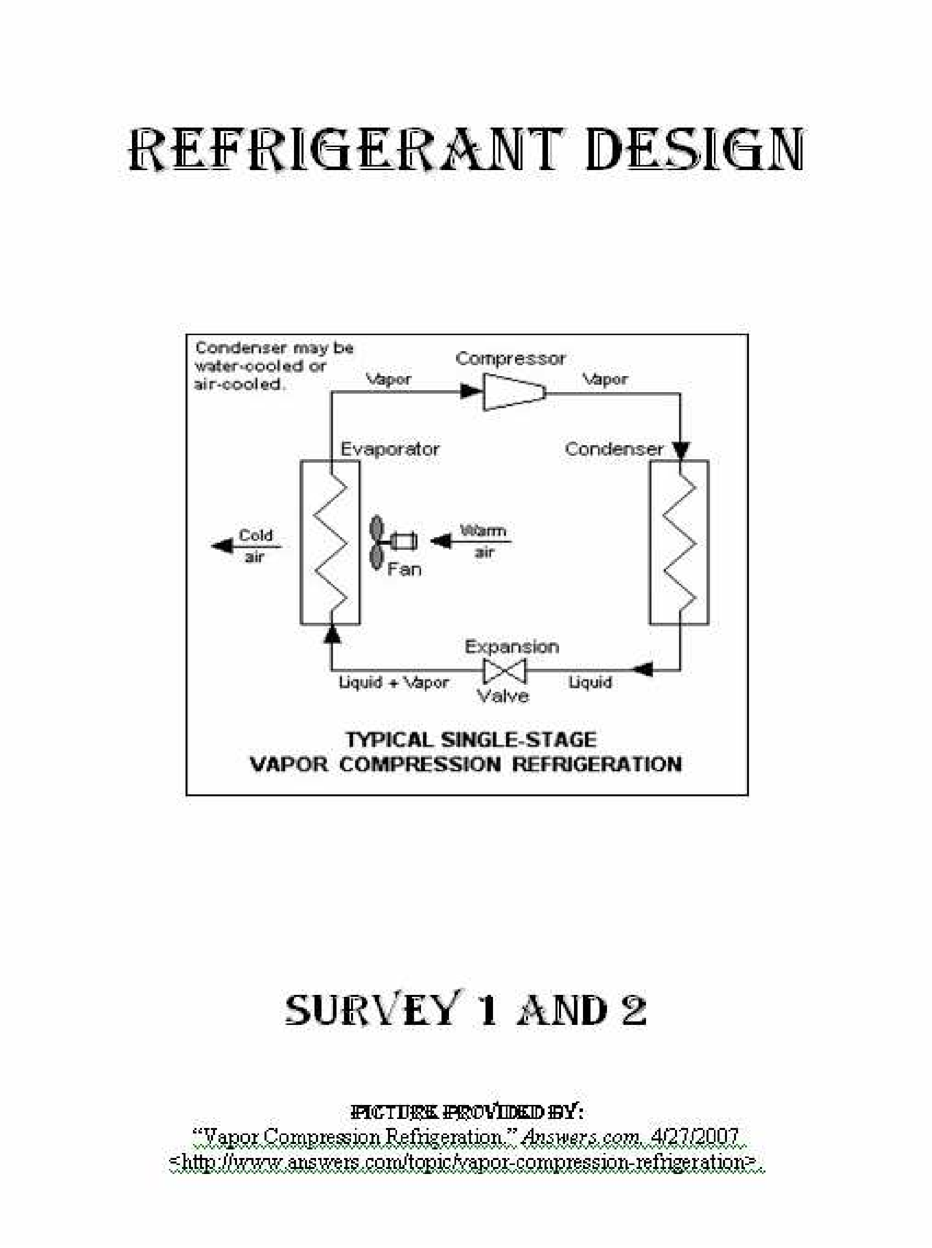
7 Appendix

7.1 Survey Developed to Predict Consumer Preference Functions



REFRIGERANT DESIGN

TYPICAL SINGLE-STAGE
VAPOR COMPRESSION REFRIGERATION

SURVEY 1 AND 2

PICTURE PROVIDED BY:
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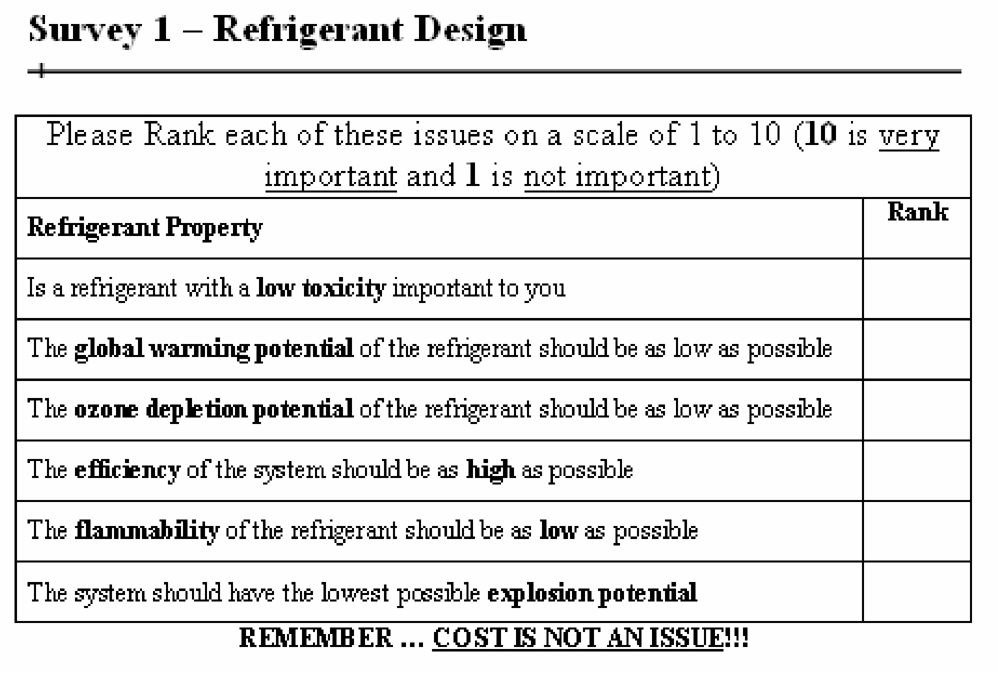
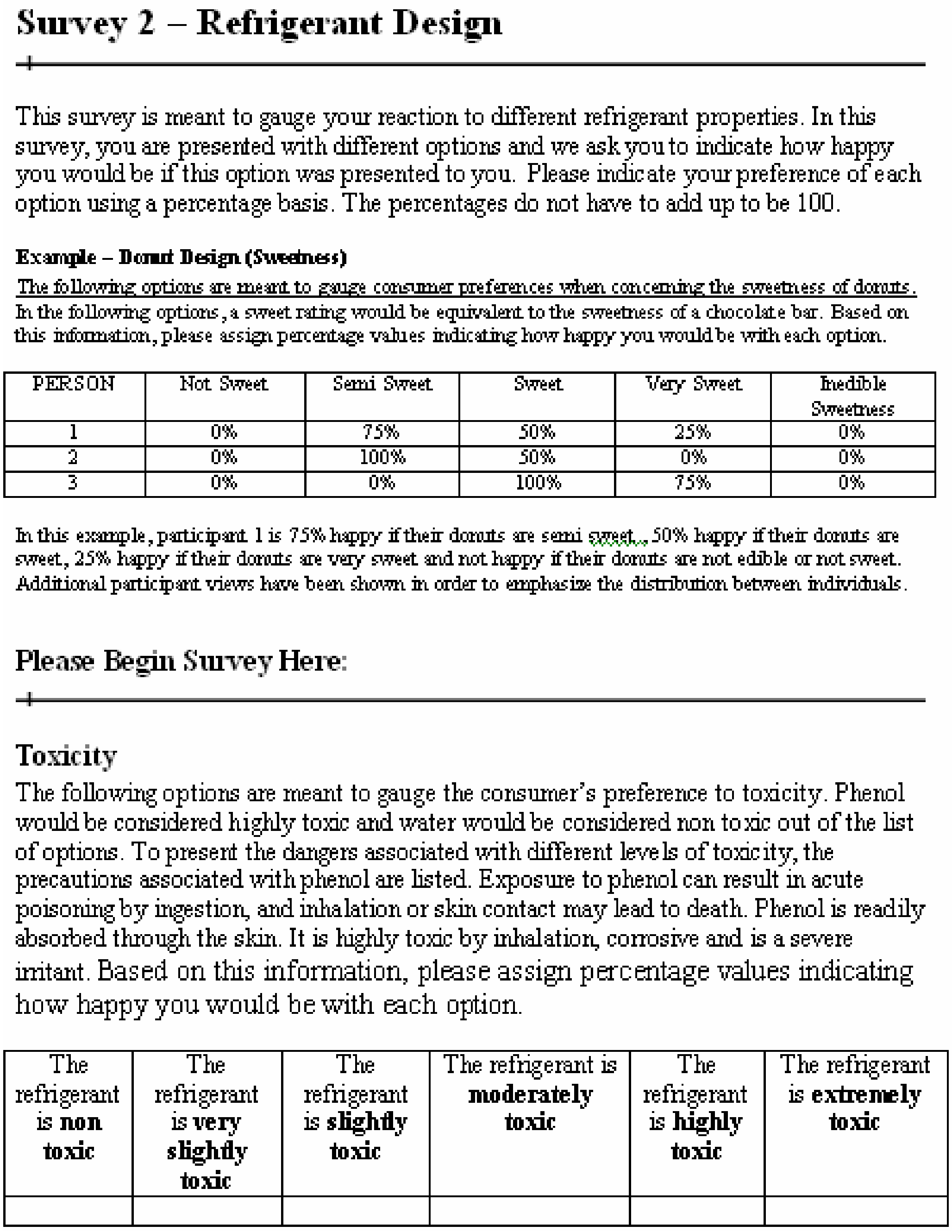


Survey 1 – Refrigerant Design

Please Rank each of these issues on a scale of 1 to 10 (**10** is very important and **1** is not important)

Refrigerant Property	**Rank**
Is a refrigerant with a **low toxicity** important to you	
The **global warming potential** of the refrigerant should be as low as possible	
The **ozone depletion potential** of the refrigerant should be as low as possible	
The **efficiency** of the system should be as **high** as possible	
The **flammability** of the refrigerant should be as **low** as possible	
The system should have the lowest possible **explosion potential**	

REMEMBER … COST IS NOT AN ISSUE!!!



Survey 2 – Refrigerant Design

This survey is meant to gauge your reaction to different refrigerant properties. In this survey, you are presented with different options and we ask you to indicate how happy you would be if this option was presented to you. Please indicate your preference of each option using a percentage basis. The percentages do not have to add up to be 100.

Example – Donut Design (Sweetness)

The following options are meant to gauge consumer preferences when concerning the sweetness of donuts. In the following options, a sweet rating would be equivalent to the sweetness of a chocolate bar. Based on this information, please assign percentage values indicating how happy you would be with each option.

PERSON	Not Sweet	Semi Sweet	Sweet	Very Sweet	Inedible Sweetness
1	0%	75%	50%	25%	0%
2	0%	100%	50%	0%	0%
3	0%	0%	100%	75%	0%

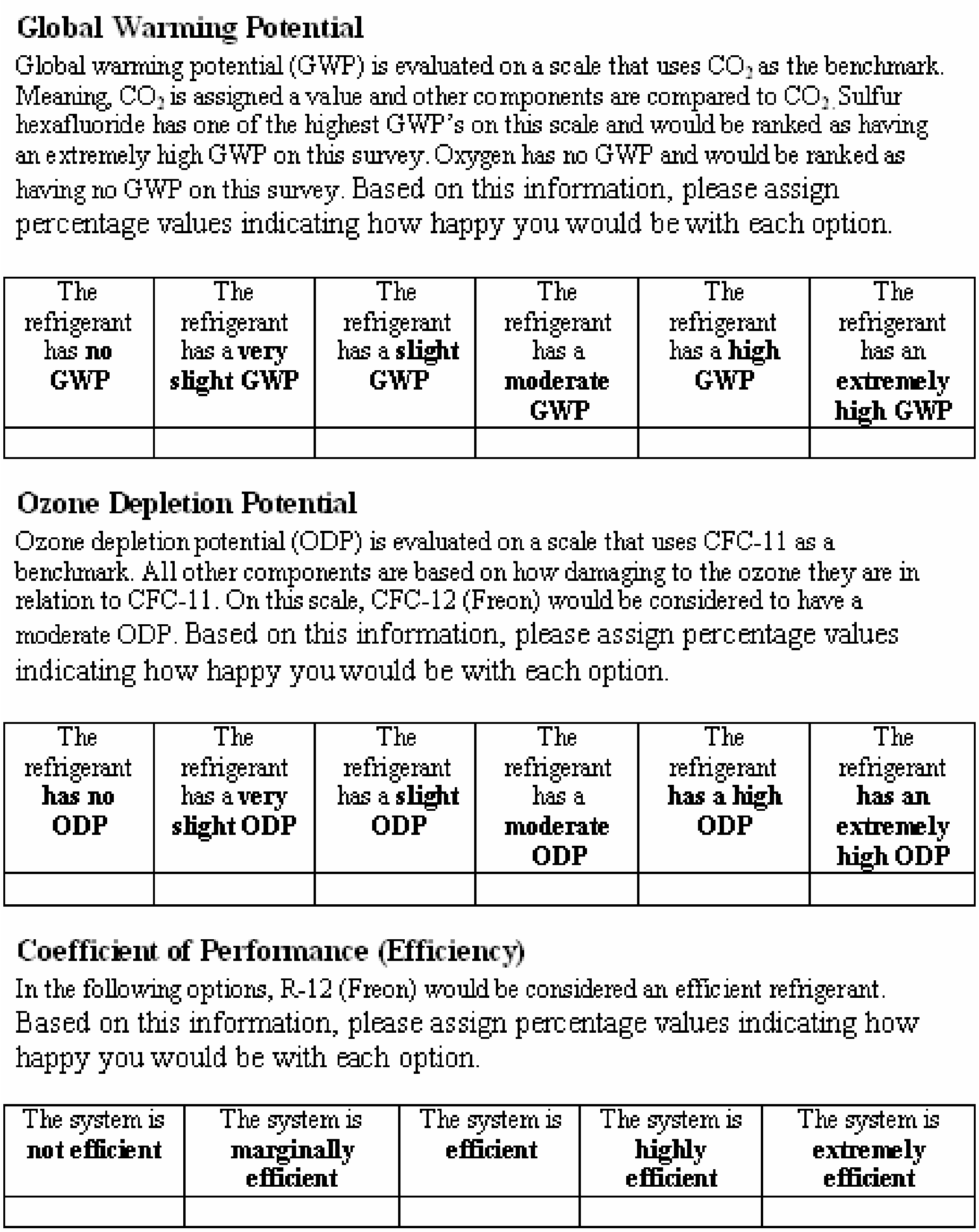
In this example, participant 1 is 75% happy if their donuts are semi sweet., 50% happy if their donuts are sweet, 25% happy if their donuts are very sweet and not happy if their donuts are not edible or not sweet. Additional participant views have been shown in order to emphasize the distribution between individuals.

Please Begin Survey Here:

Toxicity

The following options are meant to gauge the consumer's preference to toxicity. Phenol would be considered highly toxic and water would be considered non toxic out of the list of options. To present the dangers associated with different levels of toxicity, the precautions associated with phenol are listed. Exposure to phenol can result in acute poisoning by ingestion, and inhalation or skin contact may lead to death. Phenol is readily absorbed through the skin. It is highly toxic by inhalation, corrosive and is a severe irritant. Based on this information, please assign percentage values indicating how happy you would be with each option.

The refrigerant is **non toxic**	The refrigerant is **very slightly toxic**	The refrigerant is **slightly toxic**	The refrigerant is **moderately toxic**	The refrigerant is **highly toxic**	The refrigerant is **extremely toxic**



Global Warming Potential

Global warming potential (GWP) is evaluated on a scale that uses CO_2 as the benchmark. Meaning, CO_2 is assigned a value and other components are compared to CO_2. Sulfur hexafluoride has one of the highest GWP's on this scale and would be ranked as having an extremely high GWP on this survey. Oxygen has no GWP and would be ranked as having no GWP on this survey. Based on this information, please assign percentage values indicating how happy you would be with each option.

The refrigerant has **no GWP**	The refrigerant has a **very slight GWP**	The refrigerant has a **slight GWP**	The refrigerant has a **moderate GWP**	The refrigerant has a **high GWP**	The refrigerant has an **extremely high GWP**

Ozone Depletion Potential

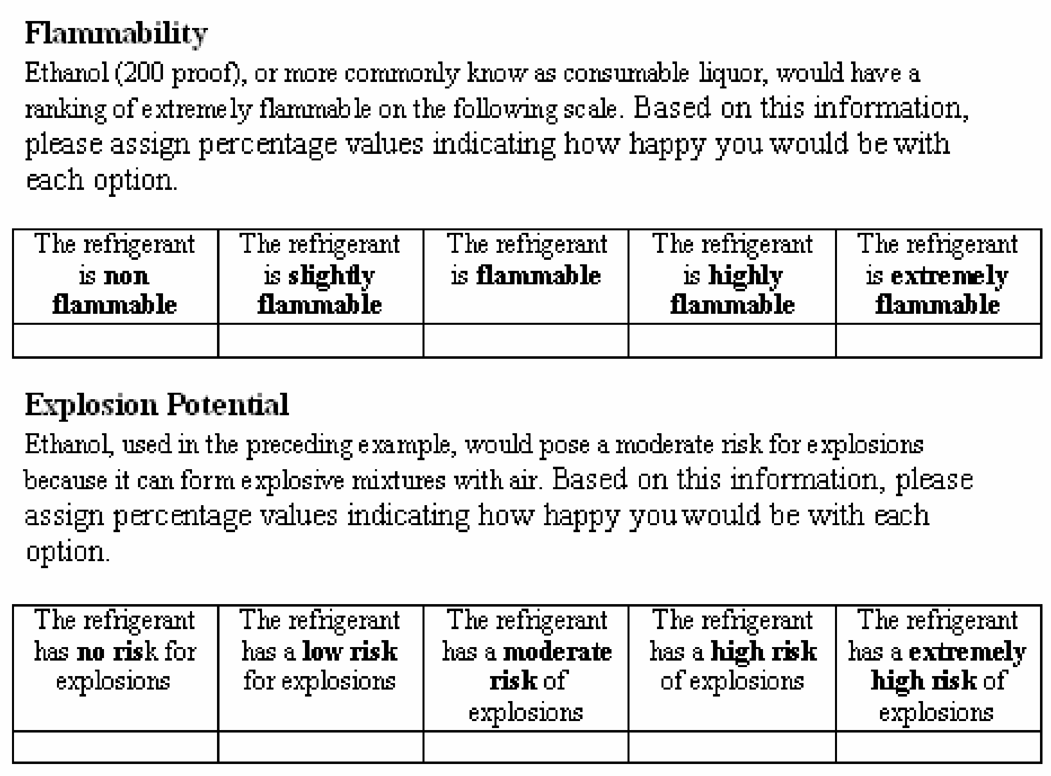
Ozone depletion potential (ODP) is evaluated on a scale that uses CFC-11 as a benchmark. All other components are based on how damaging to the ozone they are in relation to CFC-11. On this scale, CFC-12 (Freon) would be considered to have a moderate ODP. Based on this information, please assign percentage values indicating how happy you would be with each option.

The refrigerant **has no ODP**	The refrigerant has a **very slight ODP**	The refrigerant has a **slight ODP**	The refrigerant has a **moderate ODP**	The refrigerant **has a high ODP**	The refrigerant **has an extremely high ODP**

Coefficient of Performance (Efficiency)

In the following options, R-12 (Freon) would be considered an efficient refrigerant. Based on this information, please assign percentage values indicating how happy you would be with each option.

The system is **not efficient**	The system is **marginally efficient**	The system is **efficient**	The system is **highly efficient**	The system is **extremely efficient**



Flammability

Ethanol (200 proof), or more commonly know as consumable liquor, would have a ranking of extremely flammable on the following scale. Based on this information, please assign percentage values indicating how happy you would be with each option.

The refrigerant is **non flammable**	The refrigerant is **slightly flammable**	The refrigerant is **flammable**	The refrigerant is **highly flammable**	The refrigerant is **extremely flammable**

Explosion Potential

Ethanol, used in the preceding example, would pose a moderate risk for explosions because it can form explosive mixtures with air. Based on this information, please assign percentage values indicating how happy you would be with each option.

The refrigerant has **no risk** for explosions	The refrigerant has a **low risk** for explosions	The refrigerant has a **moderate risk** of explosions	The refrigerant has a **high risk** of explosions	The refrigerant has a **extremely high risk** of explosions

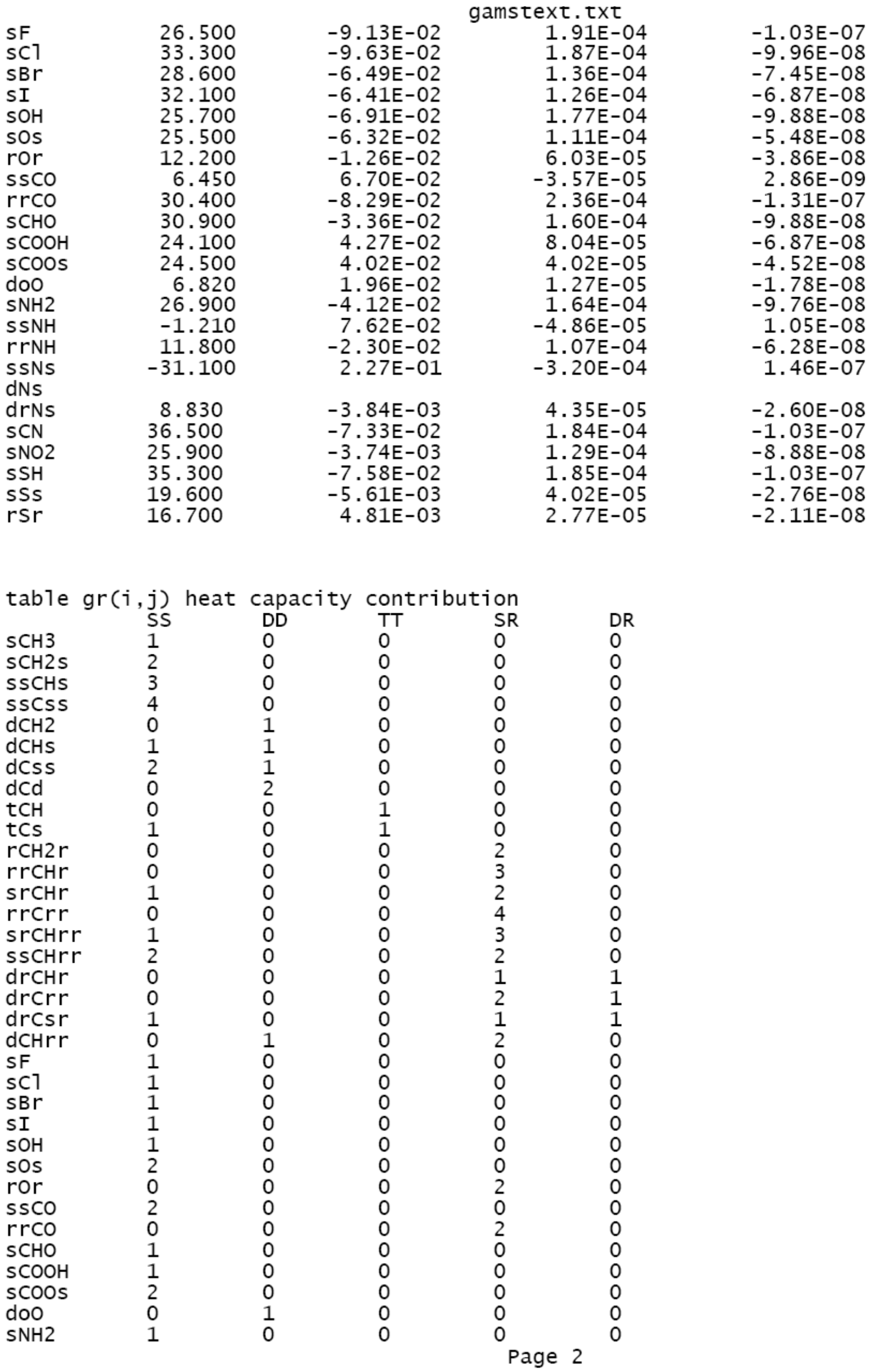
7.2 Code used in the User Interface (GAMS)

GAMS Code

The following code is used with a user interface for a non-linear mixed integer solver to maximize the objective function dH/Cp. This code incorporates all of the many of the same constraints outlined for the VBA module, with the difference that there are no extra constraints built into the code for the purpose of speeding up the process of finding the optimum refrigerant.

```
sets
         i all possible groups / sCH3,sCH2s,ssCHs,ssCss,dCH2,dCHs,dCss,
dCd,rCH2r,rrCHr,rrCrr,drCHr,drCrr,sF,sCl,sBr,sI,sOH,sOs,rOr,ssCO,
rrCO,sCHO,sCOOH,sCOOs,doO,sNH2,ssNH,rrNH,ssNs,dNs,drNs,sCN,sNO2,sSH,sSs,rSr/
         k thermodynamic labels / Tbi , Tci, Pci/
         l heat capacity contribution / Cp0Ai, Cp0Bi, Cp0Ci, Cp0Di/
         j bond types / SS, DD, TT, SR, DR/;
table c(i,k) group contribution to molecular thermodynamics
              Tbi          Tci           Pci
sCH3         23.58        0.0141       -0.0012
sCH2s        22.88        0.0189        0.0000
ssCHs        21.74        0.0164        0.0020
ssCss        18.25        0.0067        0.0043
dCH2         18.18        0.0113       -0.0028
dCHs         24.96        0.0129       -0.0006
dCss         24.14        0.0117        0.0011
dCd          26.15        0.0026        0.0028
rCH2r        27.15        0.0100        0.0025
rrCHr        21.78        0.0122        0.0004
rrCrr        21.32        0.0042        0.0061
drCHr        26.73        0.0082        0.0011
drCrr        31.01        0.0143        0.0008
sF           -0.03        0.0111       -0.0057
sCl          38.13        0.0105       -0.0049
sBr          66.86        0.0133        0.0057
sI           93.84        0.0068       -0.0034
sOH          92.88        0.0741        0.0112
sOs          22.42        0.0168        0.0015
rOr          31.22        0.0098        0.0048
ssCO         76.75        0.0380        0.0031
rrCO         94.97        0.0284        0.0028
sCHO         72.20        0.0379        0.0030
sCOOH       169.09        0.0791        0.0077
sCOOs        81.10        0.0481        0.0005
doO         -10.50        0.0143        0.0101
sNH2         73.23        0.0243        0.0109
ssNH         50.17        0.0295        0.0077
rrNH         52.82        0.0130        0.0114
ssNs         11.74        0.0169        0.0074
dNs          74.60        0.0255       -0.0099
drNs         57.55        0.0085        0.0076
sCN         125.66        0.0496       -0.0101
sNO2        152.54        0.0437        0.0064
sSH          63.56        0.0031        0.0084
sSs          68.78        0.0119        0.0049
rSr          52.10        0.0019        0.0051


table d(i,l) heat capacity contribution
            Cp0Ai          Cp0Bi           Cp0Ci            Cp0Di
sCH3        19.500       -8.08E-03        1.53E-04        -9.67E-08
sCH2s       -0.909        9.50E-02       -5.44E-05         1.19E-08
ssCHs      -23.000        2.04E-01       -2.65E-04         1.20E-07
ssCss      -66.200        4.27E-01       -6.41E-04         3.01E-07
dCH2       -23.600       -3.81E-02        1.72E-04        -1.03E-07
dCHs        -8.000        1.05E-01       -9.63E-05         3.56E-08
dCss       -28.100        2.08E-01       -3.06E-04         1.46E-07
dCd         27.400       -5.57E-02        1.01E-04        -5.02E-08
rCH2r       -6.030        8.54E-02       -8.00E-06        -1.80E-08
rrCHr        8.670        1.62E-01       -1.60E-04         6.24E-08
rrCrr      -90.900        5.57E-01       -9.00E-04         4.69E-07
drCHr       -2.140        5.74E-02       -1.64E-06        -1.59E-08
drCrr       -8.250        1.01E-01       -1.42E-04         6.78E-08
```



```
                                    gamstext.txt
sF          26.500       -9.13E-02        1.91E-04        -1.03E-07
sCl         33.300       -9.63E-02        1.87E-04        -9.96E-08
sBr         28.600       -6.49E-02        1.36E-04        -7.45E-08
sI          32.100       -6.41E-02        1.26E-04        -6.87E-08
sOH         25.700       -6.91E-02        1.77E-04        -9.88E-08
sOs         25.500       -6.32E-02        1.11E-04        -5.48E-08
rOr         12.200       -1.26E-02        6.03E-05        -3.86E-08
ssCO         6.450        6.70E-02       -3.57E-05         2.86E-09
rrCO        30.400       -8.29E-02        2.36E-04        -1.31E-07
sCHO        30.900       -3.36E-02        1.60E-04        -9.88E-08
sCOOH       24.100        4.27E-02        8.04E-05        -6.87E-08
sCOOs       24.500        4.02E-02        4.02E-05        -4.52E-08
doO          6.820        1.96E-02        1.27E-05        -1.78E-08
sNH2        26.900       -4.12E-02        1.64E-04        -9.76E-08
ssNH        -1.210        7.62E-02       -4.86E-05         1.05E-08
rrNH        11.800       -2.30E-02        1.07E-04        -6.28E-08
ssNs       -31.100        2.27E-01       -3.20E-04         1.46E-07
dNs
drNs         8.830       -3.84E-03        4.35E-05        -2.60E-08
sCN        36.500        -7.33E-02        1.84E-04        -1.03E-07
sNO2       25.900        -3.74E-03        1.29E-04        -8.88E-08
sSH        35.300        -7.58E-02        1.85E-04        -1.03E-07
sSs        19.600        -5.61E-03        4.02E-05        -2.76E-08
rSr        16.700         4.81E-03        2.77E-05        -2.11E-08


table gr(i,j) heat capacity contribution
           SS       DD       TT       SR       DR
sCH3       1        0        0        0        0
sCH2s      2        0        0        0        0
ssCHs      3        0        0        0        0
ssCss      4        0        0        0        0
dCH2       0        1        0        0        0
dCHs       1        1        0        0        0
dCss       2        1        0        0        0
dCd        0        2        0        0        0
tCH        0        0        1        0        0
tCs        1        0        1        0        0
rCH2r      0        0        0        2        0
rrCHr      0        0        0        3        0
srCHr      1        0        0        2        0
rrCrr      0        0        0        4        0
srCHrr     1        0        0        3        0
ssCHrr     2        0        0        2        0
drCHr      0        0        0        1        1
drCrr      0        0        0        2        1
drCsr      1        0        0        1        1
dCHrr      0        1        0        2        0
sF         1        0        0        0        0
sCl        1        0        0        0        0
sBr        1        0        0        0        0
sI         1        0        0        0        0
sOH        1        0        0        0        0
sOs        2        0        0        0        0
rOr        0        0        0        2        0
ssCO       2        0        0        0        0
rrCO       0        0        0        2        0
sCHO       1        0        0        0        0
sCOOH      1        0        0        0        0
sCOOs      2        0        0        0        0
doO        0        1        0        0        0
sNH2       1        0        0        0        0
                                       Page 2
```

```
ssNH       2        0        0        0        0
rrNH       0        0        0        2        0
ssNs       3        0        0        0        0
dNs        1        1        0        0        0
drNs       1        0        0        0        1
sCN        1        0        0        0        0
sNO2       1        0        0        0        0
sSH        1        0        0        0        0
sSs        2        0        0        0        0
rSr        0        0        0        2        0

Parameter a(i) number of atoms in group i
/sCH3 4,sCH2s 3,ssCHs 2,ssCss 1,dCH2 3,dCHs 2,dCss 1,dCd 1,
rCH2r 3,rrCHr 2,rrCrr 1,drCHr 2,drCrr 1,sF 1,sCl 1,sBr 1,
sI 1,sOH 2,sOs 1,rOr 1,ssCO 2,rrCO 2,sCHO 3,sCOOH 4,sCOOs 3,doO 1,
sNH2 3,ssNH 2,rrNH 2,ssNs 1,drNs 1,sCN 2,sNO2 3,sSH 2,sSs 1,rSr 1/
b(i) number of bonds in each group i
/sCH3 1,sCH2s 2,ssCHs 3,ssCss 4,dCH2 1,dCHs 2,dCss 3,dCd 2,
rCH2r 2,rrCHr 3,rrCrr 4,drCHr 2,drCrr 3,sF 1,sCl 1,sBr 1,
sI 1,sOH 1,sOs 2,rOr 2,ssCO 2,rrCO 2,sCHO 1,sCOOH 1,sCOOs 2,doO 1,
sNH2 1,ssNH 2,rrNH 2,ssNs 3,drNs 2,sCN 1,sNO2 1,sSH 1,sSs 2,rSr 2/
Tavg avergage temperature of coolant
/294/
Tevp temperature at evaporation
/272/
Tcnd temperature at condensation
/316.5/
Nmax largest possible ring
/16/
*n(i) number of atoms in group i
*/sCH3 0,sF 2,sCl 1,sSH 0,sOs 0,doO 0,dCd 0, dCHs 0,ssNs 1/;
*/drCHr 6/;
Variables
n(i)     number of groups of type i
Nt
Tb       boiling temperature
Tc       critical temperture
Pc       critical pressure
Tbr      reduced temperature
Cp0a     heat capacity at standard temperature
Tavgr    reduced average temperature
Tcndr    reduced condensing temperature
Tevpr    reduced evaporating temperature
alpha
beta
omega
Cpla     liquid heat capacity
dHvb     heat of vaporization at boiling
dHve     heat of vaporization at evaporation
h
G
ka
Pvpcr    reduced vapor pressure at condensing
Pvper    reduced vapor pressure at evaporating
Pvpc     vapor pressure at condensing
Pvpe     vapor pressure at evaporating
t1       opitmization variable
t2
t3
Ya
Yc
Ym
Yr
```

```
Yss
Ydd
Ytt
Ysr
Ydr
Ysd
Yst
Yssr
Ysdr
Ydsr
aux0
aux1
aux2
aux3
aux4
aux5;
Positive variables Nt,omega,Tbr,Tavgr,Pc,Tb,Tc,Cp0a,Tcndr,Tevpr,Cpla;
Binary variables Ya, Yc,Ym,Yss,Ydd,Ytt,Ysr,Ydr,Ysd,Yst,Yssr,Ysdr,Ydsr;
integer variable n,aux0,aux1,aux2,aux3,aux4,aux5;

*********starting molecule***************
n.l('sF')=1;
n.l('sSH')=1;
n.l('dCH2')=0;
NT.l=3;
***************thermodynamics for initial molecule*******************
Tb.l= 198.21 + sum(i, n.l(i)*c(i,'Tbi'))    ;
Tc.l = Tb.l/(0.584+0.965*sum(i, n.l(i)*c(i,'Tci'))
                      -(sum(i,n.l(i)*c(i,'Tci')))**2);
Tbr.l= Tb.l/Tc.l;
Pc.l= (0.113+0.0032*sum(i, n.l(i)*a(i))-sum(i, n.l(i)*c(i,'Pci')))**(-2);
alpha.l=(-5.97214-log(Pc.l/1.013)
         +6.09648/Tbr.l+1.28862*log(Tbr.l)
         -0.1693477*Tbr.l**(6));
beta.l=(15.2518-15.6875/Tbr.l
         -13.4721*log(Tbr.l)+0.43577*Tbr.l**6);
omega.l=alpha.l/beta.l;
Cp0a.l= (sum(i,n.l(i)*d(i,'Cp0Ai'))-37.93
        +(sum(i,n.l(i)*d(i,'Cp0Bi'))+0.21)*Tavg
        +(sum(i,n.l(i)*d(i,'Cp0Ci'))-0.000391)*Tavg**2
        +(sum(i,n.l(i)*d(i,'Cp0Di'))+0.000000206)*Tavg**3)/1000;
Tavgr.l=Tavg/Tc.l;
Tevpr.l=Tevp/Tc.l;
Cpla.l=(1/4.1868)*((Cp0a.l*1000)+8.314*(1.45
                       +0.45/(1-Tavgr.l)+0.25*omega.l*(17.11
                       +25.2*((1-Tavgr.l)**(1/3)/Tavgr.l)
                       +1.742/(1-Tavgr.l)))) ;
Tcndr.l=Tcnd/Tc.l;
dHvb.l = ((1.093*8.314*Tc.l*Tbr.l)*log(Pc.l)-1.013)/(0.93-Tbr.l) ;
h.l=Tbr.l*log(Pc.l/1.013)/(1-Tbr.l);
G.l=0.4835+0.4605*h.l;
ka.l=(h.l/G.l-(1+Tbr.l))/((3+Tbr.l)*(1-Tbr.l)**2);
Pvpcr.l=EXP(-G.l/Tcndr.l*(1-Tcndr.l**2+ka.l*(3+Tcndr.l)*(1-Tcndr.l)**3));
Pvper.l=EXP(-G.l/Tevpr.l*(1-Tevpr.l**2+ka.l*(3+Tevpr.l)*(1-Tevpr.l)**3));
Pvpc.l=Pvpcr.l*Pc.l;
Pvpe.l=Pvper.l*Pc.l;
***binary***
*$ontext
Yr.l=0;
Ya.l=1;
Yc.l=0;
Ysd.l=1;
Ydr.l=0;
```

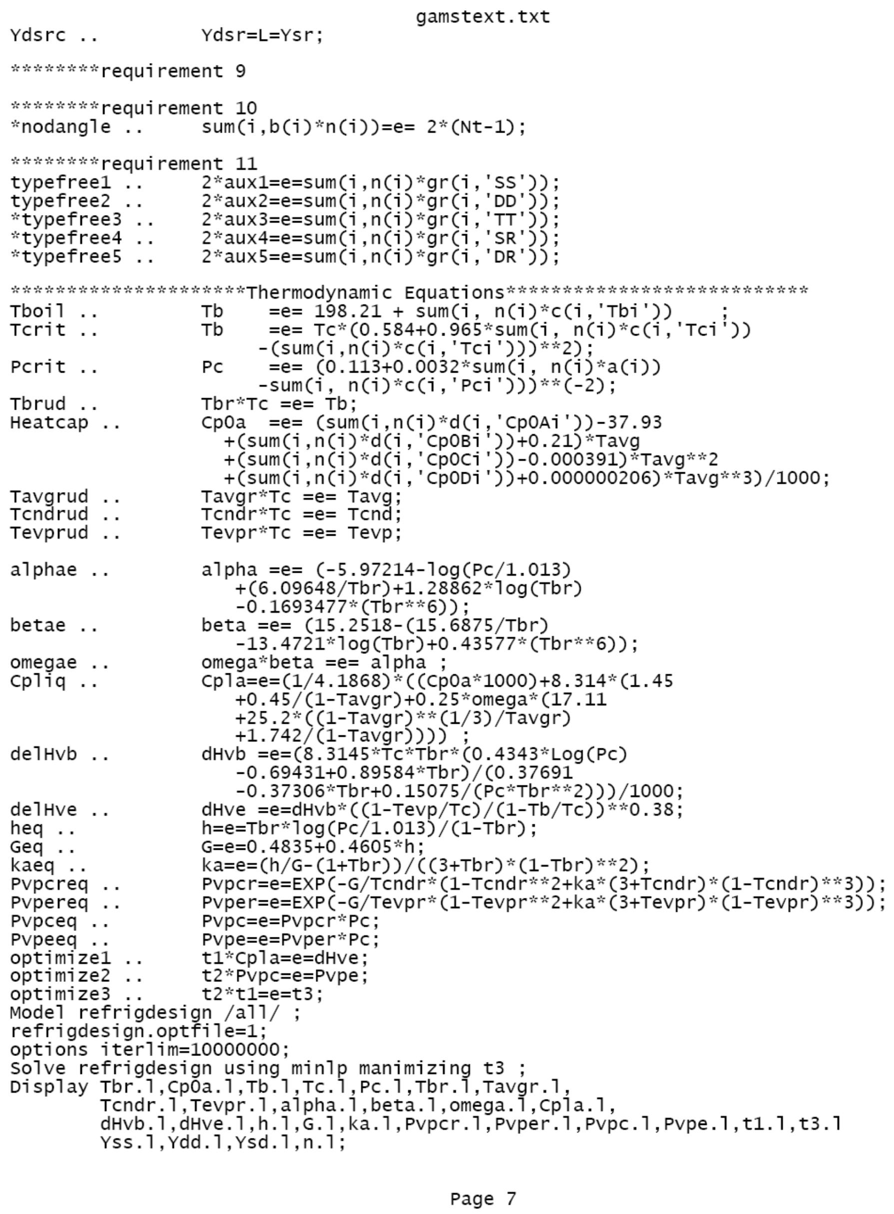
```
Yss.l=1;
*$offtext
*****************************limits************************************
Nt.lo=2;
Nt.up=7;
Tbr.lo=0.01;
Tbr.up=0.99;
Pc.lo=0.1;
Tavgr.lo=0.01;
Tavgr.up=0.99;
Tevpr.lo=0.01;
Tevpr.up=0.99;
Tcndr.lo=.01;
Tcndr.up=0.99;
Tc.lo=0.01;
Pvpcr.lo=0.000001;
Pvpcr.up=0.99;
Pvper.lo=0.000001;
Pvper.up=0.99;
Pvpe.lo=1.1;
Pvpc.lo=1.1;

Equations
Groups1    total number of groups in molecule
*Yaeq      finds the binary value for acyclic molecules
*Yceq      finds the binary value for cyclic molecules
*Ymeq1a    checks for existance of transition group acyclic
*Ymeq1b    checks for existance of transition group cyclic
*Ymeq2     checks for that a cyclic and acyclic group are in the molecule
*Yreq1     finds the binary value for cyclic molecules
*Yreq2     makes sure the ring has at least 3 groups
*Yreq3
oddfree    checks for even # of bonds (everything has something to bond with)
connect    checks for connectivity (no lone groups)
nofree     check for free bonds
Ysseq      single acyclic bond ? binary
Yddeq      double acyclic bond ? binary
*Ytteq     triple acyclic bond ? binary
Ysreq      single cyclic bond ? binary
Ydreq      double cyclic bond ? binary
Ysda       single&double transition
Ysdb       single&double transition
Ysdc
*Ysta      single&triple transition
*Ystb      single&triple transition
*Yssra     single&single cyclic transition
*Yssrb     single&single cyclic transition
*Ysdra     single&double cyclic transition
*Ysdrb     single&double cyclic transition
Ydsra      double&single cyclic transition
Ydsrb      double&single cyclic transition
Ydsrc
*nodangle
typefree1  even # of single bonds
typefree2  even # of double bonds
*typefree3 even # of triple bonds
*typefree4 even # of single cyclic bonds
*typefree5 even # of double cyclic bonds

Tboil      equation to find boiling Temperature
Tcrit      equation to find critical Temperature
Pcrit      Critical Pressure
Tbrud      Reduced boiling temperature
```

```
Heatcap    Heat capacity
Tavgrud    finds reduced temperature average
Tcndrud    finds reduced temperature of condensation
Tevprud    finds reduced temperature of evaporation
alphae
betae
omegae
Cpliq      finds liquid heat capacity
delHvb     finds heat of vaporization at boiling temperature
delHve     finds heat of vaporization at evaporation temperature
heq
Geq
kaeq
Pvpcreq    finds reduced pressure of condensation
Pvpereq    finds reduced pressure of evaporation
Pvpceq     finds pressure of condensation
Pvpeeq     finds pressure of evaporation
optimize1  optimization formula
optimize2
optimize3;
*********************Structural Constraints****************************
*********requirement 1
groups1 ..       Nt=e= sum(i, n(i));

*********requirement 2
*Yaeq ..         sign(sum(i,n(i)*gr(i,'SS'))+sum(i,n(i)*gr(i,'DD')))=e=Ya;
*Yceq ..         sign(sum(i,n(i)*gr(i,'SR'))+sum(i,n(i)*gr(i,'DR')))=e=Yc;
*Ymeq1a ..       Ym=L=Ya;
*Ymeq1b ..       Ym=L=Yc;
********requirement 3
*Ymeq2 ..        Ym=l=Ya+Yc;
********requirement 4
*Yreq1 ..        sign(sum(i,n(i)*gr(i,'SR'))+sum(i,n(i)*gr(i,'DR')))=e=Yr;
*Yreq2..         3*Yr=l=sum(i$(ord(i)>3),n(i));
*Yreq3..         sum(i,n(i)*gr(i,'SR'))+sum(i,n(i)*gr(i,'DR'))=l=Nmax*Yr;
********requirement 5
oddfree ..       sum(i,n(i)*b(i))=e=2*aux0;
********requirement 6
connect ..       sum(i,n(i)*b(i))=g=2*(Nt-1);
********requirement 7
nofree..         sum(i, n(i)*b(i))=l=Nt*(Nt-1);
********requirement 8
Ysseq ..         sign(sum(i,n(i)*gr(i,'SS')))=e=Yss;
Yddeq ..         sign(sum(i,n(i)*gr(i,'DD')))=e=Ydd;
*Ytteq ..        sign(sum(i,n(i)*gr(i,'TT')))=e=Ytt;
Ysreq ..         sign(sum(i,n(i)*gr(i,'SR')))=e=Ysr;
Ydreq ..         sign(sum(i,n(i)*gr(i,'DR')))=e=Ydr;
********requirement 8.1
Ysda ..          Ysd=e=sign(sum(i,n(i)*gr(i,'SS')*gr(i,'DD')));
Ysdb ..          Ysd=L=Ydd;
Ysdc ..          Ysd=l=Yss;
********requirement 8.2
*Ysta ..         Yst=L=Yss;
*Ystb ..         Yst=L=Ytt;
********requirement 8.3
*Yssra ..        Yssr=L=Yss;
*Yssrb ..        Yssr=L=Ysr;
********requirement 8.4
*Ysdra ..        Ysdr=L=Yss;
*Ysdrb ..        Ysdr=L=Ydr;
********requirement 8.5
Ydsra ..         Ydsr=e=sign(sum(i,n(i)*gr(i,'SR')*gr(i,'DD')));
Ydsrb ..         Ydsr=L=Ydd;
```



gamstext.txt

```
Ydsrc ..         Ydsr=L=Ysr;

********requirement 9

********requirement 10
*nodangle ..     sum(i,b(i)*n(i))=e= 2*(Nt-1);

********requirement 11
typefree1 ..     2*aux1=e=sum(i,n(i)*gr(i,'SS'));
typefree2 ..     2*aux2=e=sum(i,n(i)*gr(i,'DD'));
*typefree3 ..    2*aux3=e=sum(i,n(i)*gr(i,'TT'));
*typefree4 ..    2*aux4=e=sum(i,n(i)*gr(i,'SR'));
*typefree5 ..    2*aux5=e=sum(i,n(i)*gr(i,'DR'));

********************Thermodynamic Equations***************************
Tboil ..         Tb    =e= 198.21 + sum(i, n(i)*c(i,'Tbi'))     ;
Tcrit ..         Tb    =e= Tc*(0.584+0.965*sum(i, n(i)*c(i,'Tci'))
                      -(sum(i,n(i)*c(i,'Tci')))**2);
Pcrit ..         Pc    =e= (0.113+0.0032*sum(i, n(i)*a(i))
                      -sum(i, n(i)*c(i,'Pci')))**(-2);
Tbrud ..         Tbr*Tc =e= Tb;
Heatcap ..       Cp0a  =e= (sum(i,n(i)*d(i,'Cp0Ai'))-37.93
                   +(sum(i,n(i)*d(i,'Cp0Bi'))+0.21)*Tavg
                   +(sum(i,n(i)*d(i,'Cp0Ci'))-0.000391)*Tavg**2
                   +(sum(i,n(i)*d(i,'Cp0Di'))+0.000000206)*Tavg**3)/1000;
Tavgrud ..       Tavgr*Tc =e= Tavg;
Tcndrud ..       Tcndr*Tc =e= Tcnd;
Tevprud ..       Tevpr*Tc =e= Tevp;

alphae ..        alpha =e= (-5.97214-log(Pc/1.013)
                    +(6.09648/Tbr)+1.28862*log(Tbr)
                    -0.1693477*(Tbr**6));
betae ..         beta =e= (15.2518-(15.6875/Tbr)
                    -13.4721*log(Tbr)+0.43577*(Tbr**6));
omegae ..        omega*beta =e= alpha ;
Cpliq ..         Cpla=e=(1/4.1868)*((Cp0a*1000)+8.314*(1.45
                    +0.45/(1-Tavgr)+0.25*omega*(17.11
                    +25.2*((1-Tavgr)**(1/3)/Tavgr)
                    +1.742/(1-Tavgr)))) ;
delHvb ..        dHvb =e=(8.3145*Tc*Tbr*(0.4343*Log(Pc)
                    -0.69431+0.89584*Tbr)/(0.37691
                    -0.37306*Tbr+0.15075/(Pc*Tbr**2)))/1000;
delHve ..        dHve =e=dHvb*((1-Tevp/Tc)/(1-Tb/Tc))**0.38;
heq ..           h=e=Tbr*log(Pc/1.013)/(1-Tbr);
Geq ..           G=e=0.4835+0.4605*h;
kaeq ..          ka=e=(h/G-(1+Tbr))/((3+Tbr)*(1-Tbr)**2);
Pvpcreq ..       Pvpcr=e=EXP(-G/Tcndr*(1-Tcndr**2+ka*(3+Tcndr)*(1-Tcndr)**3));
Pvpereq ..       Pvper=e=EXP(-G/Tevpr*(1-Tevpr**2+ka*(3+Tevpr)*(1-Tevpr)**3));
Pvpceq ..        Pvpc=e=Pvpcr*Pc;
Pvpeeq ..        Pvpe=e=Pvper*Pc;
optimize1 ..     t1*Cpla=e=dHve;
optimize2 ..     t2*Pvpc=e=Pvpe;
optimize3 ..     t2*t1=e=t3;
Model refrigdesign /all/ ;
refrigdesign.optfile=1;
options iterlim=10000000;
Solve refrigdesign using minlp manimizing t3 ;
Display Tbr.l,Cp0a.l,Tb.l,Tc.l,Pc.l,Tbr.l,Tavgr.l,
        Tcndr.l,Tevpr.l,alpha.l,beta.l,omega.l,Cpla.l,
        dHvb.l,dHve.l,h.l,G.l,ka.l,Pvpcr.l,Pvper.l,Pvpc.l,Pvpe.l,t1.l,t3.l
        Yss.l,Ydd.l,Ysd.l,n.l;
```

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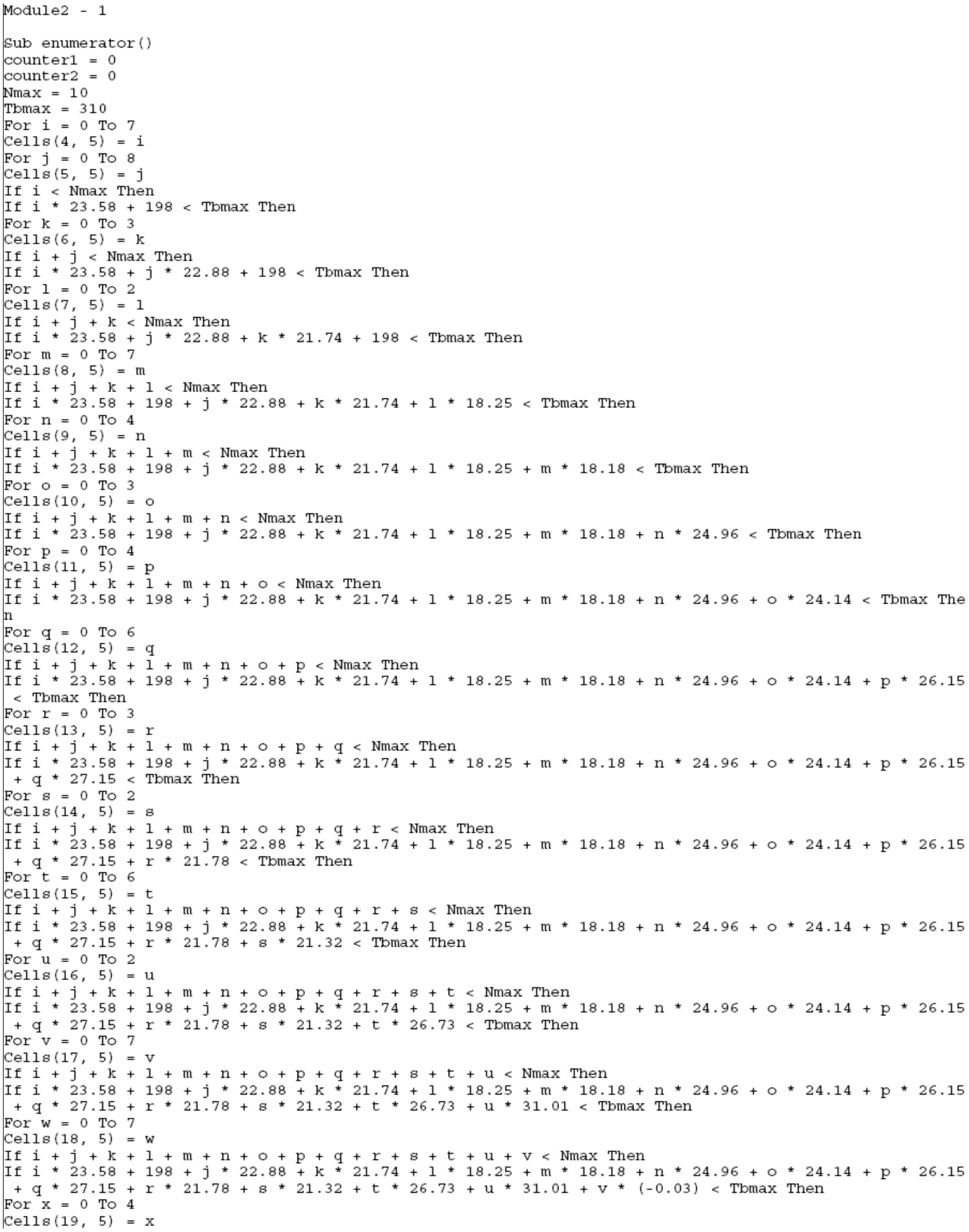
7.3 Code used in the Iterative Method in Excel

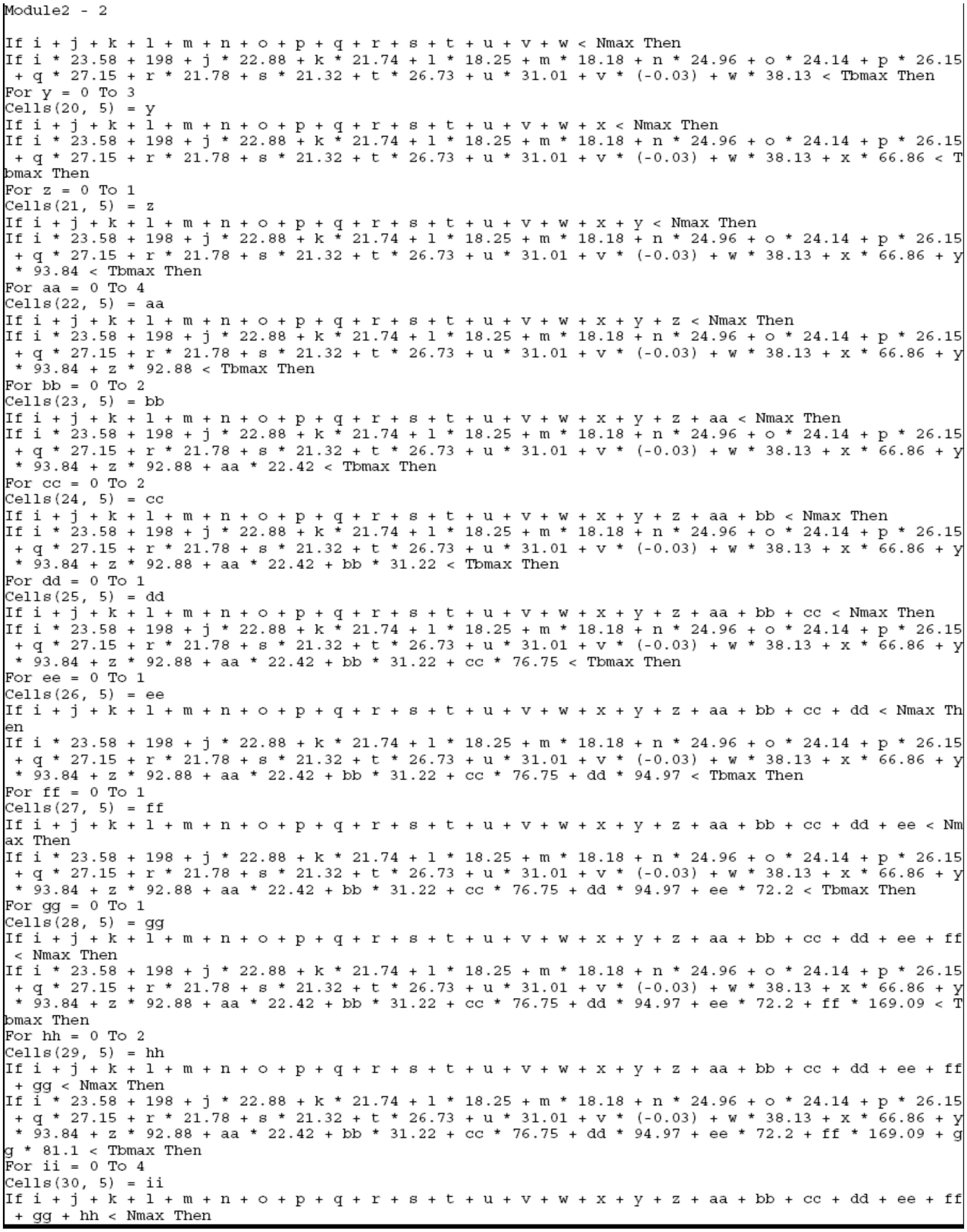
VBA Code

The following code was used in conjunction with a Microsoft Excel spreadsheet. The macro contains 39 “For…then” statements which iteratively creates every possible combination of functional groups. Within the statements, two tests speed up the macro by preventing the creation of functional group combinations that will not pass the constraints. One test excludes molecules that are larger than 10 functional groups. The second excludes that have a boiling point larger than 310K.



```
Module2 - 1

Sub enumerator()
counter1 = 0
counter2 = 0
Nmax = 10
Tbmax = 310
For i = 0 To 7
Cells(4, 5) = i
For j = 0 To 8
Cells(5, 5) = j
If i < Nmax Then
If i * 23.58 + 198 < Tbmax Then
For k = 0 To 3
Cells(6, 5) = k
If i + j < Nmax Then
If i * 23.58 + j * 22.88 + 198 < Tbmax Then
For l = 0 To 2
Cells(7, 5) = l
If i + j + k < Nmax Then
If i * 23.58 + j * 22.88 + k * 21.74 + 198 < Tbmax Then
For m = 0 To 7
Cells(8, 5) = m
If i + j + k + l < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 < Tbmax Then
For n = 0 To 4
Cells(9, 5) = n
If i + j + k + l + m < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 < Tbmax Then
For o = 0 To 3
Cells(10, 5) = o
If i + j + k + l + m + n < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 < Tbmax Then
For p = 0 To 4
Cells(11, 5) = p
If i + j + k + l + m + n + o < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 < Tbmax The
n
For q = 0 To 6
Cells(12, 5) = q
If i + j + k + l + m + n + o + p < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 < Tbmax Then
For r = 0 To 3
Cells(13, 5) = r
If i + j + k + l + m + n + o + p + q < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 < Tbmax Then
For s = 0 To 2
Cells(14, 5) = s
If i + j + k + l + m + n + o + p + q + r < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 < Tbmax Then
For t = 0 To 6
Cells(15, 5) = t
If i + j + k + l + m + n + o + p + q + r + s < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 < Tbmax Then
For u = 0 To 2
Cells(16, 5) = u
If i + j + k + l + m + n + o + p + q + r + s + t < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 < Tbmax Then
For v = 0 To 7
Cells(17, 5) = v
If i + j + k + l + m + n + o + p + q + r + s + t + u < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 < Tbmax Then
For w = 0 To 7
Cells(18, 5) = w
If i + j + k + l + m + n + o + p + q + r + s + t + u + v < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) < Tbmax Then
For x = 0 To 4
Cells(19, 5) = x
```



```
Module2 - 2

If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 < Tbmax Then
For y = 0 To 3
Cells(20, 5) = y
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 < T
bmax Then
For z = 0 To 1
Cells(21, 5) = z
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 < Tbmax Then
For aa = 0 To 4
Cells(22, 5) = aa
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 < Tbmax Then
For bb = 0 To 2
Cells(23, 5) = bb
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 < Tbmax Then
For cc = 0 To 2
Cells(24, 5) = cc
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 < Tbmax Then
For dd = 0 To 1
Cells(25, 5) = dd
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 < Tbmax Then
For ee = 0 To 1
Cells(26, 5) = ee
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd < Nmax Th
en
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 < Tbmax Then
For ff = 0 To 1
Cells(27, 5) = ff
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee < Nm
ax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 < Tbmax Then
For gg = 0 To 1
Cells(28, 5) = gg
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 < T
bmax Then
For hh = 0 To 2
Cells(29, 5) = hh
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 < Tbmax Then
For ii = 0 To 4
Cells(30, 5) = ii
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh < Nmax Then
```

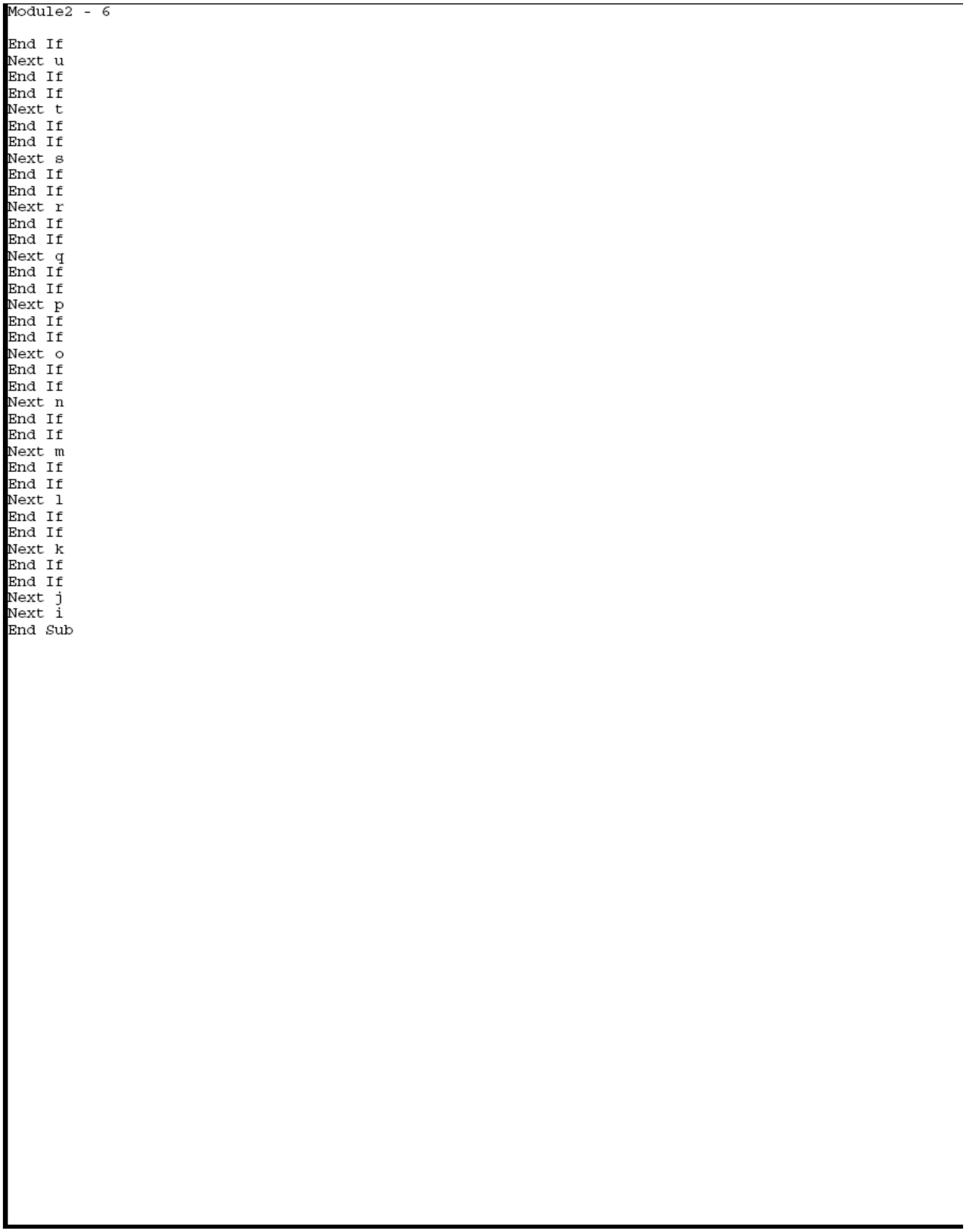
```
Module2 - 3

If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) < Tbmax Then
For jj = 0 To 5
Cells(31, 5) = jj
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 < Tbmax Then
For kk = 0 To 5
Cells(32, 5) = kk
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 < Tbmax Then
For ll = 0 To 3
Cells(33, 5) = ll
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 < Tbmax Then
For mm = 0 To 5
Cells(34, 5) = mm
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 < Tbmax Then
For nn = 0 To 2
Cells(35, 5) = nn
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll + mm < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 + mm * 57.55 < Tbmax Then
For oo = 0 To 2
Cells(36, 5) = oo
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll + mm + nn < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 + mm * 57.55 + nn * 125.66
 < Tbmax Then
For pp = 0 To 4
Cells(37, 5) = pp
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll + mm + nn + oo < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 + mm * 57.55 + nn * 125.66
 + oo * 152.54 < Tbmax Then
For qq = 0 To 4
Cells(38, 5) = qq
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll + mm + nn + oo + pp < Nmax Then
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 + mm * 57.55 + nn * 125.66
 + oo * 152.54 + pp * 63.56 < Tbmax Then
For rr = 0 To 5
Cells(39, 5) = rr
```

```
If i + j + k + l + m + n + o + p + q + r + s + t + u + v + w + x + y + z + aa + bb + cc + dd + ee + ff
 + gg + hh + ii + jj + kk + ll + mm + nn + oo + pp + qq < Nmax Then
Cells(45, 2) = counter2
If i * 23.58 + 198 + j * 22.88 + k * 21.74 + l * 18.25 + m * 18.18 + n * 24.96 + o * 24.14 + p * 26.15
 + q * 27.15 + r * 21.78 + s * 21.32 + t * 26.73 + u * 31.01 + v * (-0.03) + w * 38.13 + x * 66.86 + y
 * 93.84 + z * 92.88 + aa * 22.42 + bb * 31.22 + cc * 76.75 + dd * 94.97 + ee * 72.2 + ff * 169.09 + g
g * 81.1 + hh * (-10.5) + ii * 73.23 + jj * 50.17 + kk * 52.82 + ll * 11.74 + mm * 57.55 + nn * 125.66
 + oo * 152.54 + pp * 63.56 + qq * 68.78 < Tbmax Then
If Cells(86, 13).Value > 0 Then
e = 2
d = 134 + counter1
Cells(d, e) = Cells(93, 13).Value
Cells(d, e + 1) = Cells(86, 13).Value
Cells(d, e + 2) = Cells(4, 5).Value
Cells(d, e + 3) = Cells(5, 5).Value
Cells(d, e + 4) = Cells(6, 5).Value
Cells(d, e + 5) = Cells(7, 5).Value
Cells(d, e + 6) = Cells(8, 5).Value
Cells(d, e + 7) = Cells(9, 5).Value
Cells(d, e + 8) = Cells(10, 5).Value
Cells(d, e + 9) = Cells(11, 5).Value
Cells(d, e + 10) = Cells(12, 5).Value
Cells(d, e + 11) = Cells(13, 5).Value
Cells(d, e + 12) = Cells(14, 5).Value
Cells(d, e + 13) = Cells(15, 5).Value
Cells(d, e + 14) = Cells(16, 5).Value
Cells(d, e + 15) = Cells(17, 5).Value
Cells(d, e + 16) = Cells(18, 5).Value
Cells(d, e + 17) = Cells(19, 5).Value
Cells(d, e + 18) = Cells(20, 5).Value
Cells(d, e + 19) = Cells(21, 5).Value
Cells(d, e + 20) = Cells(22, 5).Value
Cells(d, e + 21) = Cells(23, 5).Value
Cells(d, e + 22) = Cells(24, 5).Value
Cells(d, e + 23) = Cells(25, 5).Value
Cells(d, e + 24) = Cells(26, 5).Value
Cells(d, e + 25) = Cells(27, 5).Value
Cells(d, e + 26) = Cells(28, 5).Value
Cells(d, e + 27) = Cells(29, 5).Value
Cells(d, e + 28) = Cells(30, 5).Value
Cells(d, e + 29) = Cells(31, 5).Value
Cells(d, e + 30) = Cells(32, 5).Value
Cells(d, e + 31) = Cells(33, 5).Value
Cells(d, e + 32) = Cells(34, 5).Value
Cells(d, e + 33) = Cells(35, 5).Value
Cells(d, e + 34) = Cells(36, 5).Value
Cells(d, e + 35) = Cells(37, 5).Value
Cells(d, e + 36) = Cells(38, 5).Value
Cells(d, e + 37) = Cells(39, 5).Value
Cells(d, e + 38) = Cells(40, 5).Value

Cells(d, e + 40) = Cells(65, 13).Value
Cells(d, e + 41) = Cells(66, 13).Value
Cells(d, e + 42) = Cells(67, 13).Value
Cells(d, e + 43) = Cells(68, 13).Value
Cells(d, e + 44) = Cells(69, 13).Value
Cells(d, e + 45) = Cells(70, 13).Value
Cells(d, e + 46) = Cells(71, 13).Value
Cells(d, e + 47) = Cells(72, 13).Value
Cells(d, e + 48) = Cells(73, 13).Value
Cells(d, e + 49) = Cells(74, 13).Value
Cells(d, e + 50) = Cells(75, 13).Value
Cells(d, e + 51) = Cells(76, 13).Value
Cells(d, e + 52) = Cells(77, 13).Value
Cells(d, e + 53) = Cells(78, 13).Value
Cells(d, e + 54) = Cells(79, 13).Value
Cells(d, e + 55) = Cells(80, 13).Value
Cells(d, e + 56) = Cells(81, 13).Value
Cells(d, e + 57) = Cells(82, 13).Value
Cells(d, e + 58) = Cells(83, 13).Value
Cells(d, e + 59) = Cells(84, 13).Value
Cells(d, e + 60) = Cells(85, 13).Value
Cells(d, e + 61) = Cells(86, 13).Value
```

```
counter1 = counter1 + 1
End If
End If
counter2 = counter2 + 1
End If
Next rr
End If
End If
Next qq
End If
End If
Next pp
End If
End If
Next oo
End If
End If
Next nn
End If
End If
Next mm
End If
End If
Next ll
End If
End If
Next kk
End If
End If
Next jj
End If
End If
Next ii
End If
End If
Next hh
End If
End If
Next gg
End If
End If
Next ff
End If
End If
Next ee
End If
End If
Next dd
End If
End If
Next cc
End If
End If
Next bb
End If
End If
Next aa
End If
End If
Next z
End If
End If
Next y
End If
End If
Next x
End If
End If
Next w
End If
End If
Next v
End If
```



```
Module2 - 6

End If
Next u
End If
End If
Next t
End If
End If
Next s
End If
End If
Next r
End If
End If
Next q
End If
End If
Next p
End If
End If
Next o
End If
End If
Next n
End If
End If
Next m
End If
End If
Next l
End If
End If
Next k
End If
End If
Next j
Next i
End Sub
```